Vol. XXVIII. [AUGUST, 1906.] No. 8.

THE JOURNAL

OF THE

American Chemical Society

THE ELECTRIC VACUUM FURNACE.

BY WILLIAM C. ARSEM.

Received June 4, 1906.

I. *Historical.*—Previous work *in vacuo* at high temperatures has been confined to experiments with quartz and porcelain tubes. Schuller distilled and sublimed various elements and compounds in evacuated quartz vessels. The boiling-points of many metals have been determined in evacuated porcelain tubes by Kahlbaum, Roth, Siedler, Krafft, Bergfeld, Lehmann and others. In all cases, however, the vessels were subjected to external atmospheric pressure, and the scope of the experiments was limited by the temperature at which they collapsed. Porcelain collapsed between 1400° and 1500°, and quartz at somewhat higher temperatures. Moreover, certain metals and other substances which attack quartz and porcelain could not be investigated.

In the electric vacuum furnace described below, the attainable temperature is limited only by the vaporization of carbon, and crucibles of any material suitable for a particular experiment may be used.

II. *Description.*—The vacuum furnace is a special type of resistance furnace enclosed in a vacuum chamber, with means for continuous cooling of the parts liable to be injured by excessive heating, and so designed that the effect of heat on any substance or the course of any reaction may be studied up to the vaporizing point of carbon, the substance in the crucible being always visible through a window.

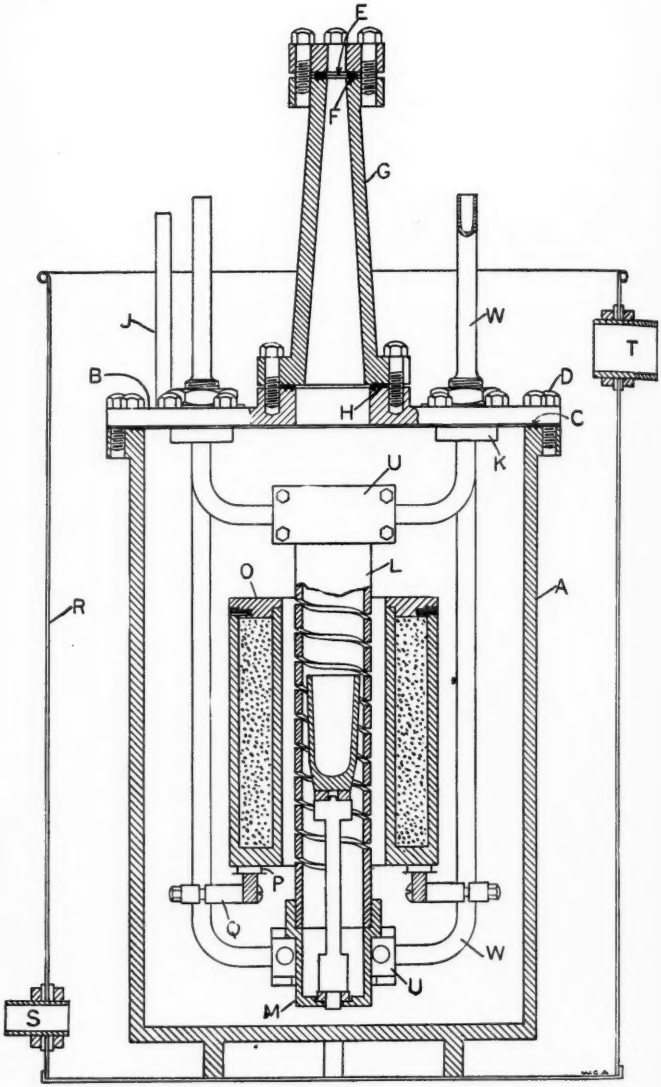


Fig. 1. Sectional elevation of electric vacuum furnace.

A calibration of the furnace to determine the relation of the temperature to the energy makes possible the accurate control of the temperature. The advantages of a vacuum for protecting the heater and the substance being heated are obvious.

It consists of an air-tight metal vessel with tubular electrodes entering the cover. These electrodes are provided with clamps which hold the heater in place and make contact between it and the electrodes. The radiation screen which surrounds the heater to diminish the radiation loss is also held in place by supports attached to the electrodes. The metal vessel stands in a can which serves as a water jacket. When the furnace is running, a constant flow of water is maintained through the water jacket and through the tubular electrodes.

The construction will be better understood from Fig. 1, which is a sectional elevation through the center. The chamber (*A*) and cover (*B*) are castings of gun-metal turned true at the joint. A lead gasket (*C*), $^1/_{16}$ inch thick, forms an air-tight joint when the cover is fastened down with the cap-screws (*D*). The first time the furnace is assembled, the tightening of the screws forces the lead into the annular grooves of the chamber and cover. The ridges thus formed in the lead washer, and suitable reference marks on the cover and chamber, make it possible to replace the parts in the same position after opening the furnace for cleaning or repairs. Leakage, due to porosity of the casting, is prevented by applying a thin coat of solder all over the inner and outer surfaces of the chamber and cover, after turning to dimensions. The chamber has four legs to permit the flow of water underneath. The tube (*J*), through which the air is exhausted, is soldered into the cover.

The window (*E*) is a disc of clear white mica about 0.005 inch thick, clamped between two lead washers (*F*) by means of a brass cap and four cap-screws. The brass surfaces touching the lead washers have annular grooves into which the lead is forced by the pressure. The window tube (*G*) is of gun-metal and is fastened to the cover by six cap-screws, the joint being made tight by a lead washer (*H*).

The electrodes (W) are formed of brass tubing bent into shape. The threaded brass bushings (K, K) which constitute parts of the electrode joints, are soldered to the electrode tubes.

The construction of an electrode joint is shown in detail in Fig. 2. Two lead washers (W_1, W_2), separated by a mica washer, are interposed between the cover and the flange of the bushing. The bushing is insulated from the cover and the upper lead washer (W_2) by the fibre sleeve (S), and the nut (N) is insulated from the cover by the fibre washer (F). The fibre parts are impregnated with paraffin to make them waterproof. By tightening the nut (N), a perfectly tight, electrically insulated joint is obtained. The heater-clamps (U, U), Fig. 1, are of copper.

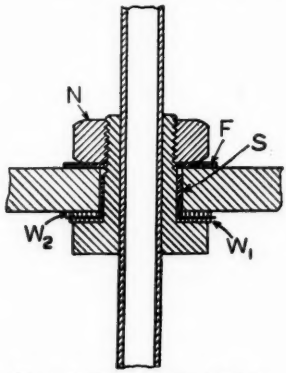


Fig. 2. Section of electrode joint.

The heater (L) is a helix of conducting material such as carbon or graphite. Artificial graphite is preferred for high temperature work because of its freedom from impurities. Metallic heaters can be used for some purposes and have certain advantages, one of which is the inability to absorb air when cold. A heater is made by sawing a slot in a hollow graphite cylinder. Its dimensions and the number of turns are so related that at the highest temperature reached the potential difference across the heater shall not be much more than 50 volts, in order to avoid excessive Edison effect and the tendency to arc across to the screen. Good results have been obtained with a heater 2 inches outside diameter, $1^5/_8$ inches inside diameter, and having ten turns in a length of $7^1/_2$ inches. The graphite cup (M) holds the lava insulating ring on which the crucible support rests. The proximity of this ring to the cold bottom of the furnace prevents it from fusing or being made conducting by heat.

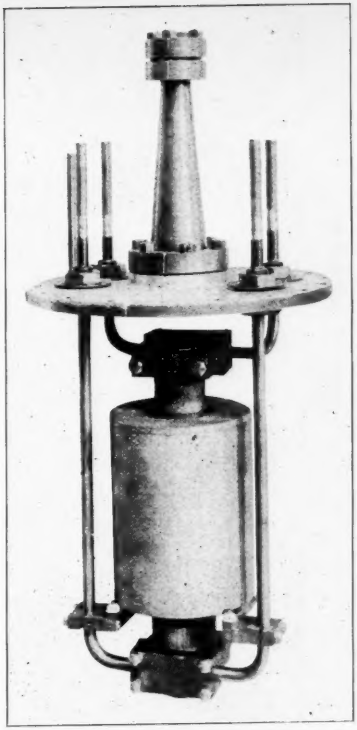


Fig. 3. Electric vacuum furnace.

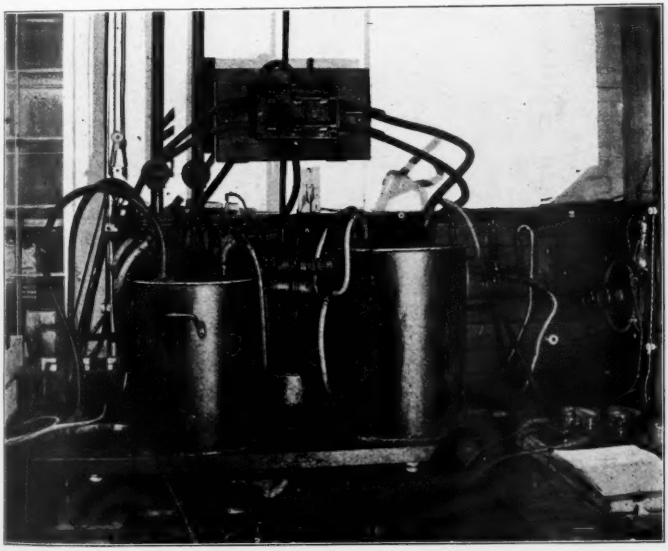


Fig. 4. Electric vacuum furnaces No. 1 and No. 2.

The radiation screen (*O*) is a double-walled cylindrical box of Acheson graphite, filled with graphite powder. Its purpose is to minimize loss of heat by radiation. Owing to the low thermal conductivity of the powdered graphite, the inner wall of the screen becomes nearly as hot as the heater, and then the rate of radiation from the heater to the screen, which depends upon the temperature difference, becomes very small, and equal to the rate at which heat is conducted away through the graphite powder. It was found that with the use of the screen, the melting-point of platinum could be reached with but one-fourth of the energy necessary without it. The screen is supported by the copper arms (*Q*) from which it is insulated by the lava buttons (*P*).

The water jacket (*R*) is a galvanized iron tank provided with an inlet (*S*) and outlet (*T*).

Fig. 3 shows the interior parts of the furnace raised out of the chamber. In Fig. 4 are shown two vacuum furnaces which have had almost constant use for two years. These have no window tubes, but the windows are fastened directly to the covers of the furnaces.

III. *Crucibles and Crucible Supports.*—The choice of material for crucibles is determined by the nature of the substance to be heated and the temperature reached. Graphite crucibles are used when the substance to be heated is not acted upon by carbon, and are conveniently made from solid rods of Acheson graphite.

Magnesia crucibles are frequently used for fusing metals and preparing alloys when the temperature to be reached does not exceed 1650°. These crucibles are made by strongly compressing in a steel mold by means of a hydraulic press, a mixture of finely powdered and sifted magnesia with a suitable binder. A porcelain kiln was used for firing the magnesia before using and for baking the crucibles, the temperature attained being about 1350° C. Crucibles made from magnesia fired at a lower temperature are very liable to crack, owing to the great shrinkage which they undergo between 1200° and 1600°.

Other metallic oxides have been found to be more suitable than magnesium oxide as crucible material. In many cases oxide crucibles must be separated from the graphite support by a refractory metal cap, to prevent reduction at the contact surface.

Crucibles of iron, copper, fire-clay, porcelain and thorium oxide have been used for special purposes, the latter substance with-

standing a higher temperature than anything else tried except graphite.

In Fig. 1, a crucible and graphite support with a metal cap are shown partly in section.

IV. *Accessory Apparatus. Vacuum Pump.*—A double-cylinder Geryk oil-pump is used with the cylinders in series. It gives a good vacuum in the furnace fifteen minutes after starting. The pump is connected to a brass main-tube having soldered branches to which the furnace, gauge, and air inlet valve are connected by means of heavy rubber pressure-tubing. The joints are made tight by brass sleeves, the ends of which are filled with a wax mixture. Brass stop-cocks were first used, but were later replaced by mercury-seal glass cocks which did not leak.

Vacuum Gauge.—A closed mercury gauge of the manometer type was used at first, but it gradually became soiled and an uncertain capillarity error was introduced, which made it unreliable for accurate measurements. To avoid this, the gauge is now connected through a tube containing glass wool and potassium bicarbonate crystals to retain dust and acid vapors, with an auxiliary tube containing a drying agent.

Electrical Apparatus.—The current is furnished by a single-phase alternator in connection with a step-down transformer. Regulation of the current is effected by means of rheostats in the generator field circuit. The measuring instruments are of the Thomson inclined-coil type. The voltage is measured directly, the current being first reduced by a current transformer.

V. *Operating Conditions. Vacuum.*—When all joints have been properly tightened, the pressure can be reduced to a fraction of a millimeter of mercury. If leaks are suspected, the furnace is closed, the jacket is filled with water and compressed air is forced into the chamber. Leaks are shown by air-bubbles. If due to defects in the casting, they can be repaired by soldering, or if not too large, by painting with pyroxylin lacquer. Leaks at the electrode-joints may occur when a new furnace is first assembled, but these disappear when the nuts are tightened sufficiently. The vacuum becomes somewhat poorer as the temperature in the furnace rises, especially with a new heater and screen, owing to the escape of gases from the graphite or from the substance which is being heated, but on maintaining the temperature at a definite point, the vacuum finally improves up to the starting value.

A high vacuum can be maintained even at the vaporizing point of graphite.

Description of Run.—The crucible is placed on the support and centered so that it does not touch the heater, the window tube is then fastened down, the washer and contact surfaces having been first carefully cleaned. When a good vacuum has been established the current is switched on and the water allowed to flow at such a rate through the jacket that it comes out barely warm, the water-level being above the window joint. Water is also passed through the electrode tubes, the outflow being allowed to play against the side of the window tube. In most cases the current should be raised gradually, so that the behavior of the heated substance can be followed.

The substance or article being heated is observed through the mica window, colored glass being used to protect the eyes at temperatures above 1100° C. At 2500° C. and above, three or more thicknesses of blue glass are necessary to make it possible to distinguish the outlines of the substance, because of the intensity of the light.

When the desired result has been obtained, the circuit is opened. From one to three hours are allowed for cooling, according to the temperature reached, then the water is let out of the jacket, air is admitted to the furnace, the window tube is unfastened and the crucible is removed.

VI. *Temperature Estimation.*—Owing to the small total heat capacity of the heater and screen, the temperature very soon reaches a constant value for each value of the energy used, and it is therefore possible to calibrate the furnace so that the relation of temperature to energy is known.

For this purpose the melting-points of copper and platinum were taken as fixed points, and the amounts of energy required to maintain these temperatures continuously were determined, the procedure being as follows:

Some pieces of electrolytic copper were fused in a graphite crucible so as to obtain oxygen-free copper with the melting-point 1084° (Holborn and Day). The current and voltage were read just when fusion began. The current was then diminished until the copper solidified and then gradually raised about one ampere every five minutes until the copper melted again. This

procedure was repeated a number of times, and the product of the lowest average values of the current and voltage was taken as the energy corresponding to the melting-point of the copper. Fusion of the globule was characterized by the appearance of a dark spot on top, this being the only part of the globule which reflected no light vertically upward. Freezing of the globule was accompanied by the disappearance of the dark spot when the copper crystallized and the surface was no longer smooth.

A piece of chemically pure platinum wire was heated in a small cup of thorium oxide inside of a graphite crucible. The current was very gradually raised as the melting-point was approached, this having been approximately determined previously. The readings were taken while beads of melted platinum were slowly forming on the wire. The melting-point of platinum was taken as 1780° C. (Le Chatelier).[1]

To find a mathematical relation between the energy and temperature the observed values were tried in various well-known formulae, and it became evident that only an exponential equation would answer.

The expression chosen was $y^n = ax$, in which y represents the temperature of the crucible above that of the room, x is the energy in kilovolt-amperes, and n and a are constants. For convenience the equation was used in the form $(y-20)^n = ax$, or $n \log (y-20) = \log a + \log x$ in which y is the actual temperature centigrade of a crucible at the middle of the heater, the average temperature of the water in the jacket at the start, 20°, being taken as the temperature of the surroundings.

The average values found by the experiments described were:

Temperature. (20°)	Kilo-volt-amperes. (0.0)
1084°	1.909
1780	4.953

From these values the constants were calculated:

$$n = 1.895$$
$$\log a = 5.4552$$
$$a = 285200$$

[1] Recent work gives the melting-point as 1710° by the thermoelectric couple (Harker: Chem. News, 91, 250 (1905); Holborn and Henning: Ber. Berl. Akad. 1905, p. 316) and 1745° by optical methods. Nernst and Wartenberg: Verh. deut. phys. Ges. 1906, p. 48.—EDITOR.

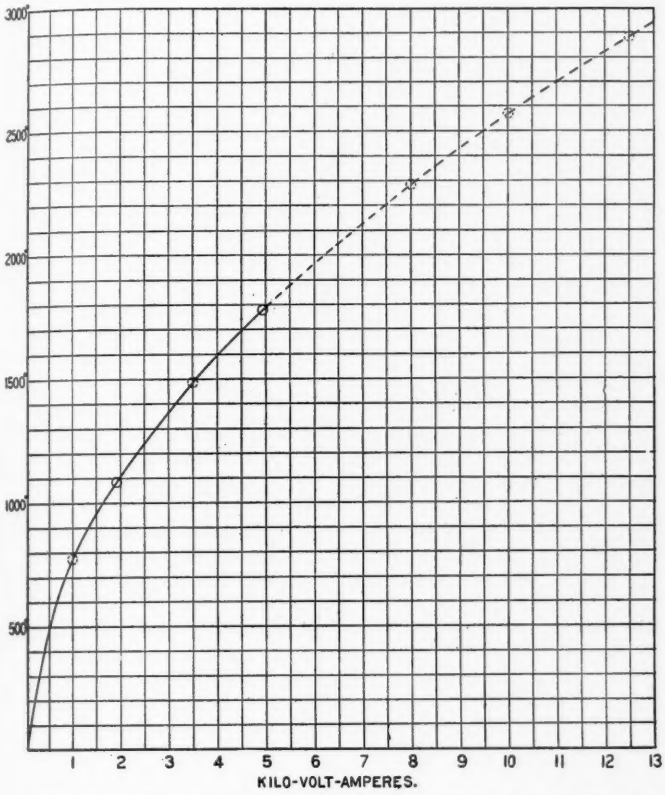


Fig. 5. Curve showing relation of temperature to energy in electric vacuum furnace.

The curve (Fig. 5) was plotted from the results obtained, the dotted portion being continued through extrapolated points calculated from the equation.

Accuracy of Calibration.—The principal source of error was the slight variation of the generator voltage. The variation at the melting-point of platinum was 4.915 to 4.992 K. V. A., corresponding to an uncertainty of 25° in temperature.

If the equation holds at higher temperatures, the error thus introduced into the constants will make measurements in the neighborhood of 3000° uncertain by 50°.

I hope later to check these calculations by an optical pyrometer, which should give accurate results, since any substance heated in the furnace, being enclosed by walls at the same temperature, will radiate like a black body.

The calibration up to 2000° is at least sufficiently accurate for practical purposes. In one experiment, the furnace was running constantly day and night for ninety hours, keeping the temperature very close to 1800°.

(No correction was made for the small current which flows through the water between the electrodes.)

VII. *Edison Effect.*[1]—In one of the first forms of the furnace, the radiation screen was supported by the lower clamp, and the crucible support was also in electrical contact with the clamp, as

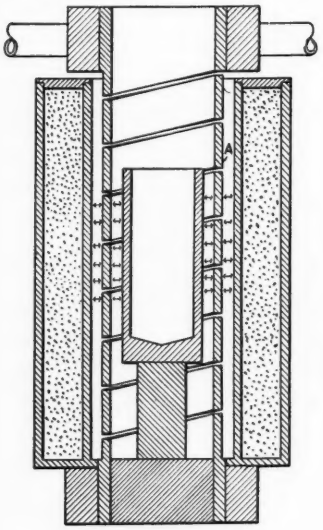


Fig 6. Arrangement of furnace No. 1, giving single-ring "Edison effect."

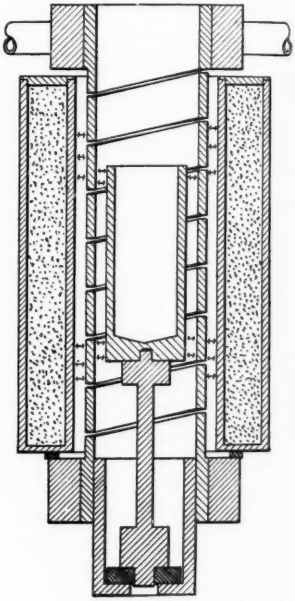


Fig. 7. Arrangement of furnace No. 1, giving double-ring "Edison effect."

shown in Fig. 6, the need for further insulation being then unknown. With such an arrangement a rise of current and a

[1] T. A. Edison, 1884. Preece: Pr. Roy. Soc. 38, 219 (1885): Fleming: Pr. Roy. Soc. 47, 118 (1889).

simultaneous fall of voltage was observed as the temperature approached 2000° C. and an arc would soon start at the point *A*, Fig. 6. This was found, by the arrangement shown in Fig. 8,

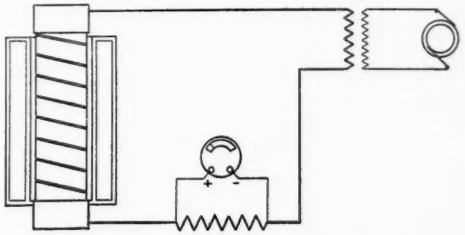


Fig. 8. Connections for showing "Edison effect."

to be due to a discharge taking place across the space between the heater and the screen. The heater being at a slightly higher temperature than the inside of the screen, an excess of current flowed across the space in such a direction that the heater was negative, and amounted to two amperes at times. The arrangement was first calibrated by passing a direct current through the shunt and meter in parallel, and noting the reading of the meter for each value of the current.

In a later form of the furnace, with the screen and crucible support both completely insulated from the heater (Fig. 7), a similar variation was observed but of much smaller magnitude, and there was now no tendency to arc across. The relative variation in the two cases is shown in Fig. 9. The paths of the discharge in the two cases is shown by the arrows in Figs. 6 and 7, and by the black coatings found on the heater, screen and crucible after a high temperature run.

The ease with which ionization takes place at high temperatures is thus shown in a striking manner.

In Fig. 10, *b* and *c* show the deposit produced on the heater and crucible at high temperatures, with the arrangement shown in Fig. 6. The location of the arc is shown in *a*, Fig. 10, the black deposit being brushed off to show clearly the disintegration which has taken place. Fig. 11 shows two crucibles with the double-ring deposit obtained with the furnace arranged as in Fig. 1 or Fig. 7.

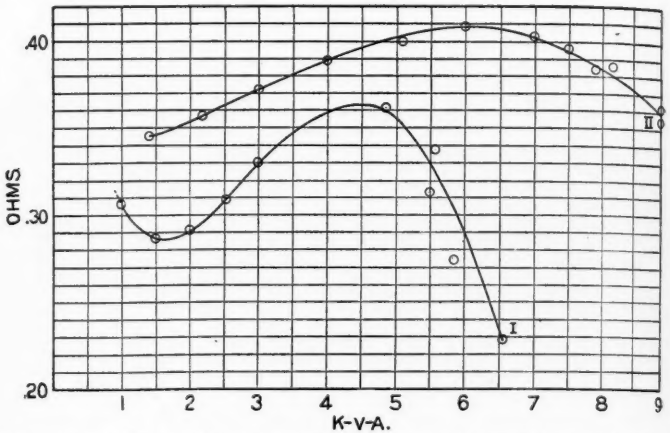


Fig. 9. Curves showing variation of resistance of heaters with temperature, for two arrangements of furnace shown in Figs. 6 and 7.

To pass a discharge through a rarefied gas as in a "vacuum tube" requires a certain fall of potential, mainly at the cathode. During the passage of the discharge, the cathode is disintegrated, the detached particles moving normally from the surface of the cathode, and depositing on the nearest surface.

It is well-known that the cathode fall diminishes as the temperature of the cathode is raised.[1] When the cathode becomes hot enough to have an appreciable vapor-pressure, the glow discharge becomes an arc.[2]

We therefore have in the furnace a complete analogy to the phenomena in a vacuum tube. The points between which the small arrows are placed become alternately anode and cathode to the alternating current, which leaks between them through the ionized gas, so that the erosion takes place on both surfaces. The gradual apparent lowering of the resistance of the heater with rise of temperature shown by the curves in Fig. 9, is due to the increasing leakage of current across the space where the arrows are. With the furnace arranged as in Fig. 7 there are two discharges in series. Between the two rings there was not a great enough potential difference to maintain two discharges.

Two explanations are possible for the presence of the rings.

[1] Cunningham: Phil. Mag. 9, 193.

[2] Hittorf: Ann. Physik. 21, 90 (1884).

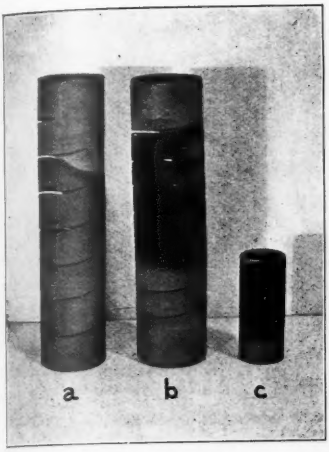


Fig. 10. Two heaters and crucible showing single-ring "Edison effect," and arc spot.

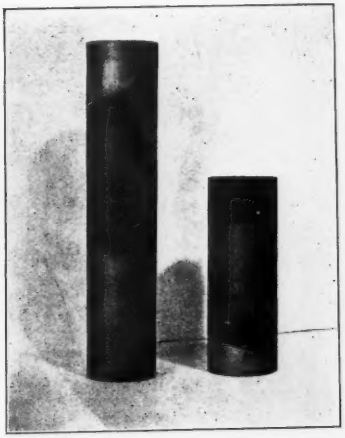


Fig. 11. Two crucibles showing double-ring "Edison effect."

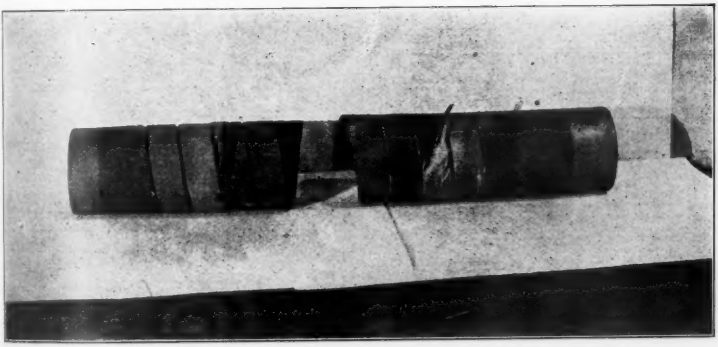


Fig. 12. Graphite heater after high temperature run.

(1) A certain minimum potential difference is required to produce a discharge at a given temperature, just as there is for an arc. This minimum is then just half that across the unblackened space on the heater between the rings, and lies between 10 and 15 volts.

(2) The resistance along the path taken by the discharge may be less than the resistance of the heater between the rings.

The second explanation seems inadequate, as it does not account for the complete absence of deposit between the rings. I consider the first explanation more satisfactory.

In the type of furnace shown in Fig. 1 the Edison effect is much reduced by using a heater of lower resistance, so that a lower voltage is required to reach a given temperature, and by making the space between the heater and screen wider. Both the screen and the crucible support are insulated from the heater. The black rings of deposit are now produced only at the highest temperatures (2500° to 3000°).

VIII. *Applications and Results.*—The furnace is especially useful for the fusion or heating of substances at temperatures beyond the range of the ordinary gas-furnace but which cannot be conveniently handled in the arc-furnace because of the excessively high and unmanageable temperature and the presence of carbon vapor. The temperature can be kept constant within less than 25° for any length of time. It makes many experiments possible at high temperatures in the absence of chemically active gases.

Above 2200° work is somewhat restricted by the lack of a crucible material which does not fuse or vaporize, or is not attacked by carbon or the substance to be heated.

Metals obtainable only in the form of a powder containing impurities can be brought into a pure compact state by fusion *in vacuo*, as the non-volatile impurities form a separate layer, and the volatile ones can pass off. Other substances which cannot be heated in air without oxidizing can be fused *in vacuo* without difficulty, unless they vaporize below their melting-points. Aluminum oxide, platinum and other refractory metals have been fused. Magnesium oxide, iron, silicon and aluminum have been vaporized.

Alloys of exact composition can easily be prepared by fusing

their components together. In this way a number of iron alloys have been made.

Chemical reactions, syntheses and reductions can be carried on with great facility under direct observation. Gas-producing reactions can be followed closely by means of the manometer, which shows the temperature at which the reaction begins, and the point at which the reaction is over.

The calibration of an optical pyrometer could be easily performed by comparing it with an electrical resistance pyrometer or a thermocouple heated in the furnace, since any substance heated in the furnace, being enclosed by walls at the same temperature, will give "black body" radiation.

Melting-points of metals, compounds, fire-brick, and other refractory substances can be determined within a few degrees by reference to the calibration curve of the furnace, and still greater accuracy could be obtained with an optical pyrometer.

Substances could be distilled for purification or separation. Magnesium, zinc and cadmium have been thus distilled.

IX. *Vaporization of Graphite, and Life of Heaters.*—At high temperatures the middle of the graphite heater slowly vaporizes, and the sublimed graphite condenses on the colder parts of the heater and radiation screen. Finally the heat tends to become more localized at some thin spot, which rapidly wastes away until a break occurs and an arc starts. This point is indicated by a sudden *drop* in voltage, because the arc so extends itself that one or more turns are short-circuited.

Fig. 12 shows a broken heater with the partly loosened skin of sublimed graphite. This sublimed graphite has an almost silvery whiteness, and under a low-power microscope shows a botryoidal surface.

The average life of a heater at different temperatures is shown by the following table:

Temp.	Life.	
2500	9 hours.	These results are for hand-sawed heaters.
2700	3¼ "	Machine-cut heaters being more uniform will probably have a somewhat longer life.
2900	2 "	
3000	1 "	
3100	¾ "	

Since carbon vaporizes from the anode of a carbon arc at about 3700° C., at atmospheric pressure, it is to be expected that *in*

vacuo it would vaporize at a much lower temperature. It is therefore very probable that the temperature measurements calculated from the extrapolated part of the curve are fairly accurate, and not overestimated, as had been feared.

In this connection it is of interest to note that Sir Wm. Crookes[1] has calculated from certain assumptions that carbon has zero vapor pressure at 3000° Abs., or approximately 2700°, which is about the temperature (estimated from the calibration curve) at which a more rapid wasting of the heater becomes noticeable.

X. *Conclusion.*—I believe that this furnace opens up a wide field for investigation of high temperature phenomena under exact and easily controlled conditions, and hope that eventually it will enable us to become familiar with the properties of substances up to extremely high temperatures.

I expect soon to be able to give the results of a number of interesting investigations which are now in progress.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.

ELECTRIC SMELTING AT SAULT STE. MARIE, ONTARIO.[2]

BY E. HAANEL.

Received June 30, 1906.

INTRODUCTION.

THE disability under which the middle provinces of Canada are placed as regards the upbuilding of an iron and steel industry on account of the necessity of importing the required metallurgical coke either from the United States or the extreme east or west of Canada engaged my attention shortly after assuming the duties of my present position. Considering the fact that the provinces of Ontario and Quebec are supplied with extensive deposits of iron ore and water-powers, the utilization of these water-powers in the production of electric energy in substitution of the energy resulting from the combustion of carbon in blast-furnaces suggested itself as a possible solution of the problem of economically producing pig iron without the use of metallurgical fuel.

Fortunately, the necessity of profitably employing the electric

[1] Pr. Roy. Soc. A 76, 458 (1905).

[2] An address delivered at Ithaca, N. Y., before the American Chemical Society, Saturday, June 30, 1906.

plants erected in different parts on the Continent, especially in France, for the production of carbide, which had to be closed down as unprofitable, furnished the incentive to invent methods for applying electric energy; first, to the production of the different ferros, and subsequently to the production of pig iron and steel.

In the solution of the problem of applying electric energy to the extraction of metals from their ores Captain Stassano, in Italy, and Héroult and Keller, in France, have rendered conspicuous service. The description of the experiments made by them attracted wide attention, for it was at once seen that if by the electric process pig iron could be economically produced, such countries as Brazil, Chile, Sweden, Norway, Finland and Canada, all rich in iron ore deposits and the necessary fluxes and possessing extensive water-powers, but lacking metallurgical fuel, would be able to render themselves independent of outside sources by employing the electrothermic process for the manufacture of their iron and steel.

It was with a view of ascertaining the practicability of introducing electric smelting into Canada that the honorable Mr. Sifton, then Minister of the Interior, appointed a Commission to investigate this subject. My instructions were: To proceed to Europe for the purpose of investigating and reporting upon the different electrothermic processes employed in the smelting of iron ores and the making of the different classes of steel, now in operation or in process of development, in Italy, France and Sweden.

The special object of this investigation was the ascertainment of all facts in connection with these processes, which were necessary for determining the cost of one ton of product, the quality of the product, and cost of machinery employed and such other facts as were required for the formation of a judgment regarding the feasibility of introducing successfully in Canada electrothermic processes for the production of iron and steel.

I was directed to avail myself of all means necessary to obtain, as far as practicable, reliable and detailed information on this subject. To ascertain what patents had been issued to the different inventors of the processes of electric smelting, the countries where they had been issued, and full particulars thereof. Photographs and accurate drawings (where necessary) of the

various parts of apparatus and plants employed were to accompany my report.

The following constituted the members of the staff under my direction: Mr. C. E. Brown, E. E.; Mr. F. W. Harbord, metallurgist; Mr. Erik Nystrom, M. E.; draftsman; Mr. Thomas Cote, secretary.

The results of the investigation of the Commission have been laid down in a report entitled "Report of the Commission Appointed to Investigate the Different Electrothermic Processes for the Smelting of Iron Ores and the Making of Steel in Operation in Europe." This report has been widely distributed, copies having been sent on requisition to Russia, Germany, Italy, France, Sweden, England, Brazil, Honolulu, New Zealand, Japan, India, Canada and the United States, showing the interest taken in and desire for information on the subject of electric smelting.

The only experiments which the members of the Commission were able to witness in the electric smelting of iron ores were those made by Dr. Héroult, at La Praz, and Mr. Keller, of Keller, Leleux & Co., at Livet, France. The first was a mere trial, furnishing no reliable quantitative results; the latter, more extended experiments, continued for a number of days, were made with a very porous hematite containing 3.21 per cent. of manganese and only 0.02 per cent. of sulphur, an ore, therefore, easily reduced and easily desulphurized. Two sets of experiments were made at Livet. In the first experiment 0.475 horse-power years were required per ton of 2,000 pounds of pig iron, corresponding to an output of 5.769 tons per 1,000 horse-power days. In the second experiment 0.226 horse-power years were required per ton of product, corresponding to an output of 12.12 tons per 1,000 horse-power days. In this experiment, moreover, most of the iron produced was white, for which cold working is required and consequently less energy consumed.

The difference in output of these two experiments was so great, being more than double that of the first in the second experiment, that no conclusion could be drawn as to the amount of energy required per ton of product and Mr. Harbord, the metallurgist of the Commission, was compelled to adopt 0.350 horse-power years, the mean of the two experiments, as the probable energy required per ton of product. This would correspond to an output of 7.827 tons per 1,000 electric horse-power days.

Before, therefore, a sound judgment could be formed as to the practicability of the electrothermic process for the smelting of Canadian ores it was desirable to establish with some degree of exactitude the amount of electric energy required per ton of product and also the following important points referring to Canadian conditions, which were either not taken up or were left in doubt by the Livet experiments:

First—Can magnetite, which is our chief ore and which is to some extent a conductor of electricity, be successfully and economically smelted by the electric process?

Second—Can iron ores with comparatively high sulphur content but not containing manganese be made into pig iron of marketable composition?

Third—The experiments made at Livet with charcoal as a reducing agent in substitution for coke having failed, could the process be so modified that charcoal, which can be cheaply made from mill refuse and other sources of wood supply useless for other purposes, could be substituted for coke? This is especially important since charcoal and peat-coke constitute home products, while coal-coke for metallurgical processes requires to be imported into the provinces of Ontario and Quebec.

The settlement of these questions was of such paramount importance for the formation of a judgment as to the feasibility of introducing electric smelting of iron ores as an economic process in those provinces of Canada which lack coal for metallurgical coke, but are abundantly supplied with water-powers and iron ore deposits, that the experimental investigation of the subject by the erection of an electric smelting plant at Sault Ste. Marie, Ont., was authorized.

Description of Experimental Furnace and Electrode Holder.—The furnace, as first designed by Dr. Héroult, consisted of an iron casing $\frac{1}{4}$ inch thick, bolted to a cast-iron plate 48 inches in diameter. This casing was vertically slit to break the magnetic circuit and render the inductance as small as possible. The gap formed by this slit was bridged over by a plate of copper 10 inches wide, which was securely riveted to the iron casing (Figs. 1 and 2).

The bottom plate, which formed one of the terminals for the current, had iron rods cast in, for the purpose of insuring a good contact with the carbon paste rammed into the lower part of the casing which formed the crucible.

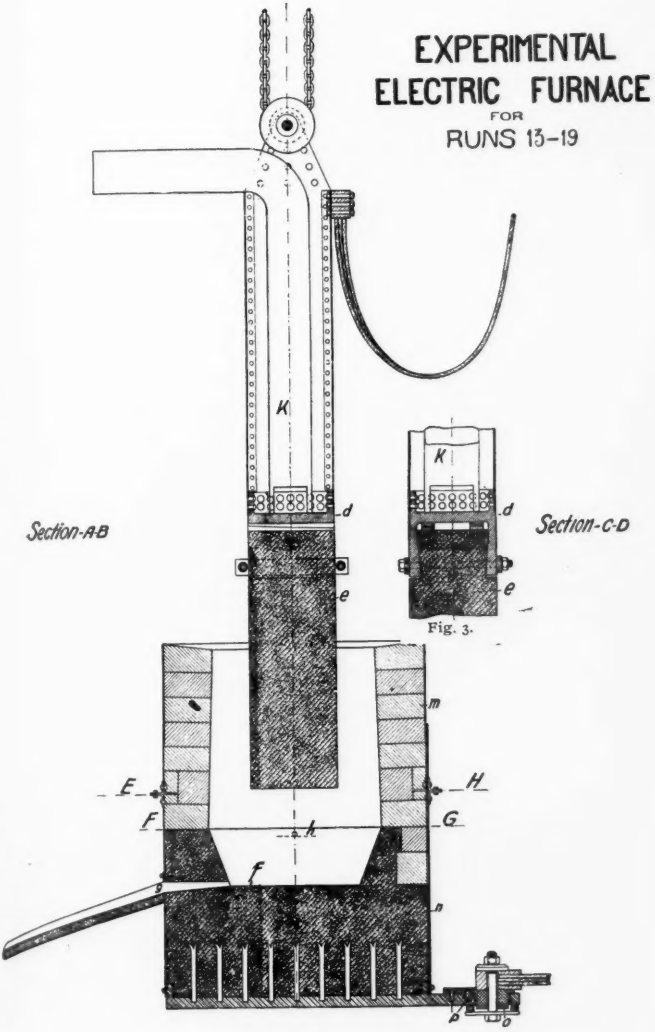

EXPERIMENTAL
ELECTRIC FURNACE
FOR
RUNS 13-19
K
d
e
Section-A-B
K
d
e
Section-C-D
m
E
H
F
G
h
f
n
p
p

Fig. 3.

Fig. 1.

The casing was made in two parts, the lower part being 3 feet and the upper 4 feet high.

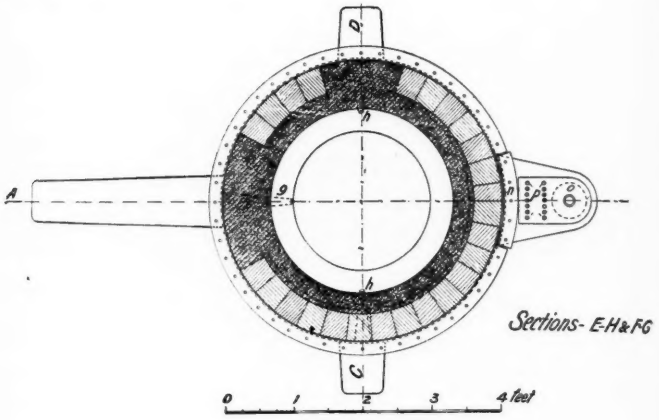


Fig. 2.

The electrode holder was made of four copper plates riveted together and to a steel shoe (*d*), Figs. 1 and 3, into which fitted the electrode (*e*). In this construction the sides of the electrode and electrode holder were flush, which allowed the holder to penetrate the charge without resistance. This was intended to permit of the consumption of the electrode to nearly its full length and obviate the necessity of throwing away from 2 to 3 feet of unused electrode, which in any other construction would be the case. To keep the contact cool a pipe (*k*) was introduced, by means of which air circulation was effected. It was found, however, that to secure proper contact between the steel shoe and electrode a clamp had to be placed around the shoe, Fig. 3, the bolts of which in descending into the charge would have offered resistance to vertical regulation of the electrode. This change in the contact rendered the long copper attachment useless.

To utilize as much of the electrode as possible, the height of the furnace was diminished to dimensions shown in Fig. 1, which represents the final modification of the furnace as used for the majority of the experiments made.

The contact did not prove entirely satisfactory, as there was a constant loss of from 2 to 3 volts, but as this loss could not be

remedied during the experiments a bolt was screwed into the electrode and connected to a voltmeter, which allowed of the determination of loss of volts by taking the difference between the volts indicated in main circuit and on the electrode.[1]

The contact with the bottom plate was at first made by driving a conical copper plug into a conical hole in the projecting part of the bottom plate and making contact by pressing the aluminium block (holding cables), copper plug and bottom plate together by means of a bolt (Figs. 1 and 2). Owing to the oxidation of the surfaces in contact, this method of making contact proved inefficient. A new contact was, therefore, made by turning a copper plug from a block of copper 10 by 12 inches, leaving an oblong flange (Figs. 1 and 2), which was dressed on both sides to make a good bearing. Two rows of holes (ϕ), Fig. 2 (14 in all), of $^3/_4$ inch diameter were drilled through the copper flange and into the bottom plate for a depth of about 1 inch, into which was run melted aluminium. This aluminium also filled any crevices which existed between the surfaces of contact.

This contact proved to be fairly satisfactory, although a loss of 1 volt or less was realized.

The lining of the furnace was given the shape of a double cone set base to base. Changes in the dimensions of the interior were made from time to time, as indicated by experience, but during the latter part of the experiments they were as follows:

	Inches.
Diameter of bottom of crucible	24
Height of lower cone	11
Height of upper cone	33
Diameter of joint base of the two cones	32
Diameter at top of furnace	30

The electrodes, manufactured by the Héroult process and imported from Sweden, were prisms of square cross-section, 16 by 16 inches by 6 feet long. The contact with the cables carrying the electric current consisted of a steel shoe riveted to four copper plates which ended in a support for a pulley. The electrode with its contact was supported by a chain passing under the pulley, one end of the chain being fastened to the wall, the other end passing over a winch operated by a worm and worm-

[1] Later an entirely new contact was made, which proved entirely satisfactory.

wheel. This formed a convenient arrangement for regulating the electrode by hand.

Electrical Machinery.—The electrical energy was furnished by one phase of a 3-phase, 400 kilowatt, 30 cycle, 2,400 volt, alternating current generator coupled by belt to a 300 horse-power, 500 volt, direct current motor. A current of 2,200 volts was delivered to an oil-cooled transformer of 225 kilowatt capacity, designed to furnish current to the furnace at 50 volts. The transformer was placed in a separate room in the furnace building, close to the furnace. From the transformer the current was led to the bottom plate contact of the furnace and to the electrode contact by conductors consisting each of 30 aluminium cables, $\frac{5}{8}$ inch in diameter.

The measuring instruments consisted of a voltmeter, an ammeter, a power-factor meter and a recording wattmeter. The transformer and electric meters were manufactured by the Westinghouse Electric and Manufacturing Company.

An additional voltmeter reading from 10 to 80 volts, supplied by the Keystone Electric Company, which proved very satisfactory, was also placed in circuit to serve as a check.

Experiments.—A number of experiments required to be made to adjust the capacity of the crucible of the furnace to the energy available and to determine the shape to be given to the interior of the furnace to insure easy passage of the charge into the reducing and melting zones. After this, attempts were made to utilize the calorific energy of the carbon monoxide resulting from the reduction of the ore, which in all experiments so far recorded had been wasted. To accomplish this, air under pressure was introduced into the furnace about 12 inches below the upper level of the charge. The carbon of the charge, in the form of coke dust, was mixed with fire-clay and briquetted to prevent it from being consumed by the air blast. It was hoped that by thus utilizing the carbon monoxide in preheating the charge and partially reducing the ore the output would be materially increased.

It was found, however, that the great heat evolved by the combustion of the carbon monoxide caused the charge to become sticky and to hang. Nor could this be remedied by stoking, the space between the walls of the furnace and the electrode being too narrow. Moreover, the electrode, although it had been protected with asbestos and iron sheeting, was found after the

experiment to have been badly corroded. The furnace was not at all adapted for these experiments and further attempts in this direction were abandoned. The experiments, however, showed that with a differently constructed furnace, in which the electrode is isolated from the charge, the output might be greatly increased by the introduction of an air blast.

The official experiments were begun about the middle of January, the furnace being in operation night and day, with some few intermissions, until the 5th of March. During that time about 150 casts were made, yielding about 55 tons of pig iron.

The following classes of ore were treated:

(1) Hematite (Negaunee).

(2) Magnetite from the Wilbur mine, Ont. (Wm. Caldwell, Esq.).

(3) Magnetite from the Blairton mine, Ont. (Pierce Co., Marmora).

(4) Magnetite from the Calabogie Mining Co. (J. G. Campbell, Esq., Perth).

(5) Magnetite from the Calabogie Mining Co. (J. G. Campbell, Esq., Perth).

(6) Magnetite from the Calabogie mine (T. B. Caldwell, Esq., Lanark).

(7) Roasted pyrrhotite from Lake Superior Corporation.

(8) Titaniferous iron ore from Quebec (J. G. Scott, Quebec).

The materials for the charge—ore, flux and carbon—were crushed to pass through a $\frac{3}{4}$ inch ring and roughly mixed. The composition of the charge in each run as given in this paper was slightly modified from time to time by varying the percentage of charcoal and flux.

Charging.—In starting the furnace a small quantity of charcoal was placed on the bottom of the crucible and the electrode lowered until an arc was developed between the charcoal and the electrode. The arc was maintained for from sixteen to twenty hours to preheat the furnace. The furnace was then filled up with the charge and by lowering or raising the electrode the current was kept as constant as possible, at 5,000 amperes.

In most experiments when charcoal was used as the reducing agent the electrode occupied a position of about 16 inches from the bottom of the crucible and required very little attention.

RUN NO. 8.[1]

Ore treated	Hematite
Reducing agent	Briquettes
Flux	Limestone

ANALYSIS OF RAW MATERIAL.

Hematite.		*Limestone.*	
SiO_2	5.42	SiO_2	1.71
Fe_2O_3	88.90	$Fe_2O_3+Al_2O_3$	0.81
Al_2O_3	2.51	$CaCO_3$	92.85
CaO	0.61	$MgCO_3$	4.40
MgO	0.30	P	0.004
Mn	0.16	S	0.052
P	0.044		99.826
S	0.002		
Loss on ignition	2.48		
	100.426		

	Per cent.
Metallic iron	62.23

The briquettes were made of 80 per cent. coke dust and 20 per cent. fire-clay.

Briquettes:

	Per cent.
Volatile matter	4.05
Fixed carbon	69.73
SiO_2	15.26
$Fe_2O_3+Al_2O_3$	8.92
CaO	0.90
MgO	0.30
S	0.84
	100.00

The charge, which was slightly modified for subsequent charges by increasing the amount of briquettes and decreasing the limestone, had the following composition:

	Pounds.
Ore	200
Briquettes	60
Limestone	50

[1] Only those runs are given which are of special interest.

ANALYSIS OF IRON PRODUCED.[1]

Cast No. 28, Grey iron.	*Cast No. 30, Grey iron.*
Total carbon..... 4.85	..... 4.35
Si..... 0.87	..... 1.03
S..... 0.018	..... 0.019

ANALYSIS OF SLAG PRODUCED.

SiO_2.....	34.40
Al_2O_3.....	15.73
CaO.....	43.53
MgO.....	2.00
Fe.....	1.35
S.....	0.55

$$\frac{\text{Slag (obtained)}}{\text{Iron (obtained)}} = \frac{1162}{2665} = 0.44$$

Length of run.....	12 hours
Mean volts on furnace	38.5
Mean amperes	4856
Power factor.....	0.919
Pig iron produced	2665 pounds
Watts=38.5 × 4856 × 0.919.....	171812
Electrical horse-power $= \frac{171812}{746} =$.....	230.3
Output of pig iron per 1,000 El. horse-power days $= \frac{2665 \times 24 \times 1000}{12 \times 230.3 \times 2000}$	11.57 tons
Electric horse-power years of 365 days per ton of pig.....	0.236

Subsequent experiments indicate that had charcoal or coke been used as a reducing agent instead of briquettes, thereby greatly reducing the amount of slag produced, the output would have been considerably increased.

RUN NO. 13.

Ore treated.....	Magnetite from Wilbur mine
Reducing agent	Charcoal
Flux.....	Sand

[1] A redetermination for the final report of the composition of slags and iron produced renders the analyses here given subject to amendment.

Wilbur Ore.

	Per cent.	
SiO_2	6.20	
Fe_2O_3	55.42	Fe=56.69
FeO	23.04	
Al_2O_3	2.56	
CaO	2.00	
MgO	6.84	
P_2O_5	0.023	P=0.01
S	0.01	
CO_2 and undet	3.907	
	100.000	

Charcoal.

	Per cent.
Moisture	14.06
Volatile matter	28.08
Fixed carbon	55.90
Ash	2.54
	100.58
Sulphur	0.058

The sand used was common furnace sand, of which no analysis was made.

COMPOSITION OF CHARGE.

	Pounds.
Ore	400
Charcoal	125
Sand	27

ANALYSIS OF IRON PRODUCED.

Cast No. 49, Grey Iron.		*Cast No. 53, Grey Iron.*	
Total carbon	5.18		4.65
Si	1.30		1.41
S	0.020		0.012
P	0.029		0.024

ANALYSIS OF SLAG PRODUCED.

SiO_2	35.84
Al_2O_3	31.80
CaO	14.39
MgO	16.22
S	0.26
Fe	0.35

$$\frac{\text{Slag}}{\text{Iron}} = \frac{4195}{12858} = 0.326$$

Length of run	61 hours, 25 min.
Mean volts on furnace	35.75
Mean amperes	5000
Power factor	0.919
Pig iron produced	12858 pounds
Watts=35.75 × 5000 × 0.919	164271
Electrical horse-power = $\frac{164271}{746}$	220.2

Output of pig iron per 1,000 El. horse-power

$$\text{days} = \frac{12858 \times 24 \times 1000}{61.4 \times 220.2 \times 2000} \quad \ldots\ldots\ldots \quad 11.41 \text{ tons}$$

El. horse-power years[1] per ton of pig..... 0.2399

RUN NO. 14.

Ore treated.....Magnetite from Blairton mine.
Reducing agent.....Charcoal
Flux..... { Limestone / Sand

ANALYSIS OF RAW MATERIAL.

Blairton Ore.

SiO_2	6.60	
Fe_2O_3	60.74	Fe=55.85
FeO	17.18	
Al_2O_3	1.48	
CaO	2.84	
MgO	5.50	
P_2O_5	0.037	P=0.016
S	0.57	
CO_2 and undet	5.053	
	100.000	

Charcoal and limestone same as in previous run.

COMPOSITION OF CHARGE.

	Pounds.
Ore	400
Charcoal	125
Limestone	25
Sand	6

ANALYSIS OF IRON PRODUCED.

Cast No. 80, Grey Iron.

Total carbon	3.73
Si	3.53
S	0.042
P	0.034

ANALYSIS OF SLAG PRODUCED.

SiO_2	33.80
Al_2O_3	10.20
CaO	21.78
MgO	30.50
S	2.05
Fe	0.25

$$\frac{\text{Slag}}{\text{Iron}} = \frac{4892}{11989} = 0.41$$

Length of run..... 65 hours, 30 min.
Mean volts on furnace..... 36.03
Mean amperes..... 4987
Power factor..... 0.919

[1] 365 days.

Pig iron produced..... 11989 pounds
Watts=36.03 × 4987 × 0.919..... 165125
Electrical horse-power = $\frac{165125}{746}$..... 221.34
Output of pig iron per 1000 El. horse-power days = $\frac{11989 \times 24 \times 1000}{65.5 \times 221.34 \times 2000}$..... 9.92 tons
El. horse-power year per ton of pig..... 0.276

RUN NO. 15.

Ore treated .....Magnetite from Calabogie[1]
Reducing agent.....Charcoal and charcoal braise
Flux .....Limestone

ANALYSIS OF RAW MATERIAL.

Calabogie Ore.

SiO_2.....	3.80	
Fe_2O_3.....	56.24	Fe=59.38
FeO.....	25.76	
Al_2O_3.....	3.73	
CaO.....	2.00	
MgO.....	3.42	
P_2O_5.....	0.85	P=0.371
S.....	0.20	
CO_2 and undet.....	4.00	
	100.00	

Limestone and charcoal the same as in previous runs. The charcoal braise used was of poor quality, being wet, high in ash and mostly fines.

The composition of the charge, when using charcoal, was:

	Pounds.
Ore.....	400
Charcoal.....	125
Limestone.....	30

When using charcoal braise, the composition of the charge was:

	Pounds.
Ore.....	400
Charcoal braise.....	145
Limestone.....	40

During this run the alternator had to be stopped on account of repair of motor. The furnace was then considerably cooled and some time was consumed before it was again in working condition.

[1] Calabogie Mining Company.

FIRST PART OF RUN—ANALYSIS OF IRON PRODUCED.

Cast No. 89, Grey iron.		*Cast No. 90, Grey iron.*	
Total carbon	3.53		3.43
Si	0.95		1.17
S	0.024		0.016
P	0.554		0.457

ANALYSIS OF SLAG PRODUCED.

SiO_2	24.30
Al_2O_3	27.16
CaO	36.06
MgO	10.74
S	1.67
Fe	0.25

$$\frac{\text{Slag}}{\text{Iron}} = \frac{1335}{4520} = 0.29$$

Length of run	23 hours, 50 min.
Mean volts on furnace	36.16
Mean amperes	5.000
Power factor	0.919
Pig iron produced	4520 pounds
Watts $= 36.16 \times 5000 \times 0.919$	166155
Electrical horse-power $= \frac{166155}{746}$	222.72
Output of pig iron per 1000 El. horse-power days $= \frac{4520 \times 24 \times 1000}{23.83 \times 222.72 \times 2000}$	10.21 tons
El. horse-power year per ton of pig	0.268

SECOND PART OF RUN—ANALYSIS OF IRON PRODUCED.

Cast No. 92, Grey iron.		*Cast No. 95, Grey Iron.*	
Si	0.73		0.95
S	0.011		0.012

$$\frac{\text{Slag}}{\text{Iron}} = \frac{892}{2722} = 0.33$$

Length of run	16 hours, 15 min.
Mean volts on furnace	35.85
Mean amperes	5000
Power factor	0.919
Pig iron produced	2722 pounds.
Watts $= 35.85 \times 5000 \times 0.919$	164730
Electrical horse-power $= \frac{164730}{746}$	220.81
Output of pig iron per 1000 El. horse-power days $= \frac{2722 \times 24 \times 1000}{16.25 \times 220.81 \times 2000}$	9.10 tons
El. horse-power year per ton of pig	0.301

RUN NO. 16.

Ore treated.....Magnetite from Calabogie[1]
Reducing agent.....Charcoal
Flux.....Limestone, Quartz

ANALYSIS OF RAW MATERIAL.

Calabogie Ore.

SiO_2	6.06	
Fe_2O_3	58.00	Fe=59.85
FeO	24.78	
Al_2O_3	1.00	
CaO	0.40	
MgO	6.00	
P_2O_5	0.046	P=0.020
S	0.17	
CO_2 and undet	3.544	
	100.000	

Charcoal.

Moisture	2.20
Volatile matter	20.60
Fixed carbon	74.40
Ash	2.80

Limestone same as in previous runs.

COMPOSITION OF CHARGE.

	Pounds.
Ore	400
Charcoal	125
Limestone	45
Quartz	5

ANALYSIS OF IRON PRODUCED.

Cast No. 102, Grey Iron.

Total carbon	4.20
Si	1.75
S	0.005
P	0.047

ANALYSIS OF SLAG PRODUCED.

SiO_2	30.90
Al_2O_3	12.30
CaO	40.09
MgO	12.91
S	1.48
Fe	0.56

$$\frac{\text{Slag}}{\text{Iron}} = \frac{2556}{7150} = 0.36$$

[1] Calabogie Mining Co., Shaft No. 4.

Length of run	38 hours, 20 min.
Mean volts on furnace	36.5
Mean amperes	4993
Power factor	0.919
Pig iron produced	7150 pounds.
Watts = $36.5 \times 4993 \times 0.919$	167483
Electrical horse-power = $\frac{167483}{746}$	224.50

Output of pig iron per 1000 El. horse-power

$$\text{days} = \frac{7150 \times 24 \times 1000}{38.33 \times 224.50 \times 2000} \quad \ldots\ldots \quad 9.97 \text{ tons}$$

RUN NO. 17.

Ore treated.....Magnetite from Calabogie mine[1]
Reducing agent.....Charcoal
Flux.....Limestone, Quartz

ANALYSIS OF RAW MATERIAL.

Calabogie Ore.

SiO_2	4.00	
Fe_2O_3	55.31	Fe = 58.29
FeO	25.20	
Al_2O_3	2.24	
CaO	2.40	
MgO	4.00	
P_2O_5	0.95	P = 0.415
S	0.45	
CO_2 and undet	5.45	
	100.00	

Charcoal same as in run No. 15. Limestone same as in previous runs.

COMPOSITION OF CHARGE.

	Pounds.
Ore	400
Charcoal	125
Limestone	20

Occasionally small quantities of quartz were added.

ANALYSIS OF IRON PRODUCED.

Cast No. 111, Grey Iron.		*Cast No. 113, Grey Iron.*	
Si	1.49		1.55
S	0.016		0.015
P	0.500		0.520

[1] T. B. Caldwell, Esq.

ANALYSIS OF SLAG PRODUCED.

SiO_2	26.96
Al_2O_3	20.64
CaO	27.40
MgO	15.50
S	1.41
Fe	0.21

$$\frac{\text{Slag}}{\text{Iron}} = \frac{3263}{8303} = 0.39$$

Length of run	43 hours, 5 min.
Mean volts on furnace	36.79
Mean amperes	5000
Power factor	0.919
Pig iron produced	8303 pounds.
Watts $= 36.79 \times 5000 \times 0.919$	169050
Electrical horse-power $= \frac{169050}{746}$	226.6
Output of pig iron per 1,000 El. horse-power days $= \frac{8303 \times 24 \times 1000}{43.08 \times 226.6 \times 2000}$	10.20 tons
El. horse-power year per ton of pig	0.268

RUN NO. 18.

Ore treated	Roasted pyrrhotite
Reducing agent	Charcoal
Flux	Limestone

ANALYSIS OF RAW MATERIAL.

Roasted Pyrrhotite.

SiO_2	10.96
Al_2O_3	3.31
Fe_2O_3	65.43
CaO	3.92
MgO	3.53
S	1.56
P	0.016
Cu	0.41
Ni	2.23
Metallic iron	45.80

Charcoal and limestone same as in previous run. The limestone in the charge was decreased from 120 pounds when starting to 50 pounds. The composition then being:

	Pounds.
Ore	400
Charcoal	110
Limestone	50

ANALYSIS OF IRON PRODUCED.

	Cast No. 125.	*Cast No. 130.*	*Cast No. 133.*
Total carbon	3.23	3.38	2.50
Si	4.90[1]	4.50[1]	6.32[1]
S	0.007	0.006	0.007
P	0.062	0.037	0.042
Cu	0.86	0.87	0.71
Ni	3.70	4.12	4.00

ANALYSIS OF SLAG PRODUCED.

SiO_2	16.44
Al_2O_3	13.86
CaO	53.25
MgO	8.80
S	5.28
Fe	0.65
Cu	trace
Ni	trace

$$\frac{\text{Slag}}{\text{Iron}} = \frac{5060}{7336} = 0.69$$

Length of run ..... 56 hours, 20 min.
Mean volts on furnace 36.05
Mean amperes 5000
Power factor 0.919
Pig iron produced (ferro-nickel) ..... 7336 pounds.
Watts = $36.05 \times 5000 \times 0.919$ 165649

$$\text{Electrical horse-power} = \frac{165649}{746} \text{ ..... } 222.05$$

Output of pig iron (ferro-nickel) per 1000 El.

$$\text{horse-power days} = \frac{7336 \times 24 \times 1000}{56.33 \times 222.05 \times 2000} \quad 7.038 \text{ tons}$$

El. horse-power year per ton of pig 0.389

RUN NO. 19.

Ore treated ..... Titaniferous iron ore
Reducing agent ..... Charcoal
Flux ..... Limestone, Fluorspar

ANALYSIS OF RAW MATERIAL.

Titaniferous Iron Ore.

SiO_2	7.12	
Fe_2O_3	30.30	Fe = 43.59
FeO	28.78	
Al_2O_3	7.00	

[1] By increasing the limestone of the charge the silicon content of the ferro-nickel pig recently produced has been depressed to 2 per cent.

CaO	1.00	
MgO	4.14	
P_2O_5	0.064	P=0.028
S	0.04	
TiO_2	17.82	
Cr_2O_3	2.50	Cr=1.42
	99.684	

Charcoal and limestone same as in previous run.

COMPOSITION OF CHARGE.

	Pounds.
Ore	400
Charcoal	100
Limestone	50
Fluorspar	50

ANALYSIS OF PIG IRON PRODUCED.

	Cast No. 136.	*Cast No. 137.*
Total carbon	...	3.50
Si	4.50	2.80
S	0.007	0.091
P	0.143	0.060
Ti (approx.)	1.00	1.30

ANALYSIS OF SLAG PRODUCED.

SiO_2	7.00
Al_2O_3	28.50
CaO	14.23
MgO	2.93
TiO_2	38.92
Fe	1.13
S	0.90

On account of the furnace being in a very bad condition, the lining being eaten away by the limy slag used in the previous run, the run had to be stopped and no figures as to output could be obtained.

The slag was very fluid and likely the fluorspar in the charge could have been reduced considerably or omitted altogether.

The iron obtained in cast No. 136 was probably mixed with some iron from the previous charge, when ore with high phosphorus content was used.

The Smelting of Magnetite.—It was expected that considerable difficulty would be experienced in the smelting of magnetite, on account of its conductivity. It was thought that with the furnace

in use, in which the electrode was immersed in the charge, the current would disseminate itself laterally from the sides of the electrode through the charge, preventing the current at the reducing and fusion zone from attaining such density as would be required for the high temperature necessary for reduction and fusion. With charcoal as a reducing agent this difficulty was not experienced, nor was the inductance of the furnace increased by the presence of magnetite.

It should, however, be mentioned that the phenomenon of rapid temporary decrease of ohmic resistance of the charge shortly after the current is put on, when the charge consists of conductors in the form of small pieces, described by J. Bronn, in his article entitled "Zur Anwendung lose geschichteter kleinstückiger Leiter für electrische Heizwiederstände,"[1] was occasionally observed in some of the runs made. This trouble occurred chiefly at the beginning of a new experiment, before the furnace had acquired its normal temperature. By adding a few shovels of iron ore, omitting flux and charcoal, it was sometimes possible to cause the electrode, which to keep the current constant had by hand regulation been elevated, to return to its normal position. In a few instances, however, this method failed, especially when the furnace was choked with fines and the gases evolved escaped under great pressure. Since the electric installation did not permit the compensation of the temporary increase of conductivity of the charge by decrease of voltage with constancy of current, the electrode in such case rose to the top of the furnace and it became necessary to melt down the charge and start anew.

If the explanation offered by Bronn is correct that the decrease of the ohmic resistance during the "Anheizungsphase" is occasioned by the more intimate contact of the conducting pieces of the charge due to pressure of escaping gases from the pores of the carbon and the carbon dioxide evolved from the limestone, it is evident that preheating the charge, which might be effected by utilizing the carbon monoxide resulting from reduction, would entirely overcome this difficulty, if the charge were sufficiently porous to permit the gases evolved to escape at low pressure. Under such conditions the electrode would maintain its normal position throughout the operation, requiring to be lowered only to keep step with its consumption.

[1] "Electrotechnische Zeitschrift," 1906, Heft 9.

The ores treated, with the exception of the hematite and the roasted pyrrhotite, contained a high percentage of magnesia, producing a very infusible slag. When the furnace had been running for some time this infusible material formed a scale around the crucible, the electric energy available not being sufficient to keep it in a molten condition. The crucible and lower part of the furnace were, therefore, partially filled up, preventing easy access of the charge to the reducing and melting zone. This slower feeding left the charcoal on top of the furnace exposed to the air a longer time, thus increasing the amount of charcoal required and decreasing the output. With a greater current than was available and consequent higher temperature, the formation of the scale would have been prevented and the output correspondingly increased.

The electric installation at our disposal was far from ideal for electric smelting experiments. Aside from the drop of voltage due to the frequent slipping of the belt connecting motor and generator, it was impossible to increase the current beyond 5,000 amperes at from 35 to 40 volts. This inelasticity of the system prevented the determination of the most suitable current and voltage for a given charge in the furnace.

The Use of Charcoal as a Reducing Agent.—It was of great importance to ascertain whether charcoal without being briquetted with the ore could be used instead of coal-coke. No difficulty whatever was experienced, in fact so admirably adapted was charcoal, when crushed to pass a $\frac{3}{4}$ inch ring, as a reducing agent in the electric furnace that coke and briquettes of coke with clay were abandoned and all the experiments with magnetite and roasted pyrrhotite described were made with charcoal. Some of the charcoal available was of very poor quality, being little better than charred wood containing only about 56 per cent. of fixed carbon. This and the fact that a considerable quantity of the charcoal was consumed on top of the furnace account for the large quantity of charcoal used per ton of product. A modification of the furnace, protecting the upper layer of the charge from the atmosphere, and the use of charcoal properly carbonized would decrease considerably the amount of charcoal which was actually used in the experiments and consequently reduce the cost of production as given.

Consumption of Electrode.—For the production of 42,711 pounds

of pig iron, 384 pounds of electrode were consumed, the same electrode having been in commission for thirteen days.

Consumption of electrode per ton of pig iron:

$$\frac{384 \times 2000}{42711} = 17.98 \text{ pounds.}$$

During the time this electrode was in commission the material in the furnace was melted down several times, exposing the red hot electrode to the oxidizing atmosphere. The consumption of electrode was found to be greater for white iron than for grey iron and since the 42,711 pounds of pig iron produced included several casts of white iron, the consumption of electrode was also on that account greater than it would have been had only grey iron been produced.

Power Factor.—The power factor of the furnace was determined by Mr. Chas. Darrall, of the Canadian Westinghouse Company of Hamilton, Ont., and was found to be 0.919. This high power factor is due to the construction of the furnace casing, as described above.

Since the true electric power is the apparent electric power multiplied by the power factor, it is evident that any error made in the determination of the power factor which tends to decrease its value will appear to decrease the consumption of energy per ton of product. The large output of 12.12 tons per 1,000 electric horse-power days, *i. e.*, the small amount of electric horse-power absorbed per ton of product in the second Livet experiments, was obtained in a furnace with the abnormally low power factor 0.564. Whatever doubt may be engendered as to the correctness of the figure obtained for the absorption of electric energy on account of this low power factor of the Keller furnace, such doubt cannot arise regarding the figures obtained with the Héroult furnace for the absorption of electric energy in the Government experiments on account of its remarkably high power factor 0.919.

Moreover, since the cost of alternate current generators increases with increase of capacity, furnaces with high power factors (which can utilize a high percentage of the capacity of the generators) will be more economical as regards the first cost of the electrical installation of an electric smelting plant than furnaces with low power factors.

Modification of Experimental Furnace for Commercial Production of Pig Iron.—Probably the largest unit which can at present be constructed on the model of the experimental furnace will not exceed 1,500 horse-power. The construction of the experimental furnace to fit it for the production of pig iron on a commercial scale will require to be modified in the following important particulars:

(1) The top of the furnace requires to be modified to permit of the application of labor-saving machinery for charging.

(2) Provision requires to be made for the collection and utilization of the carbon monoxide produced by the reduction of the ore; this involves also the protection of the charcoal of the charge from combustion on top of the furnace.

The greater capacity insuring less loss of heat by radiation and the modification of the furnace to permit of the utilization of the carbon monoxide will materially increase the output beyond that ascertained by the experimental furnace. The experiments indicated that under *normal* conditions about 11.5 tons were produced by an expenditure of 1,000 electric horse-power days (see runs Nos. 8 and 13). It is, therefore, not unreasonable to assume that under similar conditions with a properly constructed plant the output per 1,000 horse-power days would certainly reach 12 tons. This figure has been adopted in calculating cost of production per ton of pig.

The protection of the charcoal of the charge from combustion on top of the furnace will materially decrease the amount of charcoal necessary for reduction and consequently lessen the cost of this item. This saving has, however, not been taken into account in the estimate of cost.

On account of the value of the product, the smelting of roasted nickeliferous pyrrhotite by the electrothermic process, as carried out with the Government experimental plant, admits of immediate commercial application without other modification of the furnace than increase of its capacity.

The Lake Superior Corporation has acquired the Government plant by purchase and employs it for the semi-commercial production of ferro-nickel pig. The company has had the furnace in operation night and day since about March 7th. The smelting operations are left entirely in the hands of the workmen, who had been trained during the progress of the Government ex-

periments. I am informed that the furnace works with admirable regularity, the regulation of the electrode requiring hardly any attention, and the output is of excellent and uniform quality.

The Electric Furnace as Compared with the Blast-Furnace.—The tendency among iron manufacturers for some time has been to increase the size and capacity of blast-furnaces until the enormous capacity of 600 to 800 tons per day with a furnace stack 100 feet high has been reached.

But for the economical working of a blast-furnace there is a point beyond which the furnace can be neither increased nor decreased in size. It seems to have been established that furnaces with a height of 90 feet and corresponding output prove the most economical. While fuel is cheap and ore of good quality and high iron content is still abundant, any disadvantages of such large units will not be felt. It may, however, be of value to call attention to some of the disadvantages connected with the employment of large units. These are as follows:

First—Large first cost of furnace.

Second—Excessive cost of charging machinery and upkeep of same.

Third—Large expense and probable idleness through breakdown.

Fourth—Cost of and difficulties of making repairs, relining, etc.

Fifth—Serious complications resulting from scaffolding, involving loss of life and money.

Sixth—Financial loss resulting from wrong composition of charge, involving many tons of iron before correction can be made.

Yet, with even these drawbacks the blast-furnace of to-day, representing the result of a hundred years' experience and inventive skill, must be pronounced a perfect machine, hardly permitting further improvement, and if the electric furnace, which is yet in its infancy, is able in its present state of development to compete with a blast-furnace under the special conditions of cheap electric energy and high price of metallurgical fuel, what may we not expect of its performance when all the calories available in an electric furnace will have been utilized by proper design, as the result of years of experience?

It is, therefore, scarcely to the point to speak of faults or disadvantages of a new invention, which, as they are realized, may be corrected, but it is of great importance to point out any advantages

a new apparatus may possess over a long-tried machine. The following are some points in favor of the electric furnace:

First—Original small cost of furnace.

Second—Absence of bulky or costly charging machinery.

Third—Small expense involved through breakdown.

Fourth—Small cost and ease with which repairs may be made.

Fifth—No serious complications arising from scaffolding.

Sixth—Loss due to wrong composition of charge reduced to a minimum.

Seventh—Perfect control of the temperature in the reducing and melting zone.

In reviewing the advantages arising from the introduction of the electric furnace, it must be understood that a smelting plant operated by electricity is composed of several small units, the disablement of any one of which will not render the plant idle.

Again, in case of accident, such a furnace will cool down in a comparatively short time, permitting repairs to be made in the least possible time.

General Remarks.—The far-reaching consequence of the gratifying results achieved by these experiments will at once be apparent. Many of our magnetites are too high in sulphur to be handled by the blast-furnace and consequently have so far been of no commercial value. But the very best of pig iron, as has been proven, can be made from ores which contain as high as 1.5 per cent. of sulphur. A blast-furnace will not usually handle an ore which contains more than 0.1 per cent. of sulphur and requires, therefore, an ore which cannot be obtained at a low figure.

Regarding the water-power required for the application of this process it may be stated that many water-powers exist in Ontario and Quebec, surrounded by iron ore fields, in localities ill adapted for the application of electric energy for any other purpose and could be developed to furnish an electric horse-power year for from $4.50 to $6.00.

With such a price for the energy required, the small consumption of electrode, the cheapness of the ore employed and the peculiar excellence of the pig iron produced, electric smelting of iron ores in Canada, using charcoal or peat-coke made from our peat bogs of enormous extent, may be pronounced commercially feasible.

Under the prevailing conditions in Canada it now only remains for the engineer to design a plant on a commercial scale, say of 100 to 150 tons daily output, with all the necessary labor-saving appliances. Just as in the case of the blast-furnace so likewise with the electric furnace, experience gained will result in further economy and the day may not be far distant when the carbon monoxide, which is of high calorific value and which at present as a product of the reaction taking place in the electric furnace is allowed to escape without utilization, will be employed for increasing the output by something like one-fourth. When this is accomplished, the blast-furnace could not compete with the electric furnace, even under conditions where coke might be cheaper than at present quoted in Ontario and Quebec.

With the present advance which has been made in the transmission of electric energy, batteries of electric furnaces could be set up at various iron ore deposits, which could be fed with electric energy from some centrally located water-power, thus effecting a saving of the transportation costs of the ore from the mine to the furnace.

The following is a summary of the results of the experiments which have been made under Government auspices at Sault Ste. Marie:

First—Canadian ores chiefly magnetite can be economically smelted by the electrothermic process.

Second—Ores of high sulphur content can be made into pig iron containing only a few thousandths of a per cent. of sulphur.

Third—The silicon content can be varied as required for the class of pig to be produced.

Fourth—Charcoal which can be cheaply produced from mill refuse or wood which could not otherwise be utilized and peat-coke made from peat can be substituted for coke without being briquetted with the ore.

Fifth—A ferro-nickel pig can be produced practically free from sulphur and of fine quality from roasted nickeliferous pyrrhotite.

Sixth—Pyrite cinders, resulting from the roasting of pyrite in the manufacture of sulphuric acid and which at present constitute a waste product, can be smelted into pig iron by the electric process.

Seventh—Titaniferous iron ores containing up to 5 per cent. can be successfully treated by the electrothermic process. This conclusion is based upon an experiment made with an ore containing 17.82 per cent. of titanic acid, yielding a pig iron of good quality.

The results of the introduction of electric smelting into countries possessing iron ore deposits and water-powers but lacking metallurgical fuel may be summarized as follows:

First—The utilization of water-powers which cannot at present be profitably employed for any other purpose.

Second—The utilization of iron ore deposits, which on account of their high sulphur content cannot be treated by blast-furnace methods and have so far been valueless. This is of extreme importance, for already the question has arisen, how long the present supply of blast-furnace iron ore is likely to last and ores are now accepted by furnace men with a metallic content such as would not have been looked at a few years ago, and when these ores are exhausted and none but sulphurous ores or titaniferous ores are available, the stacks of the numerous blast-furnaces, which have rendered such magnificent service to our present civilization, will be silent and smokeless, having been supplanted by the electric furnace which can successfully treat an ore which the blast-furnace cannot handle.

Third—The utilization of peat bogs for the production of peat coke, to be used as reducing material for the operation of electric furnaces, and utilization of mill refuse and sawdust, for which there has so far been no practical use.

Fourth—Rendering such countries independent of fuel import for metallurgical processes.

Fifth—Enabling them to produce their own pig iron for home consumption and consequently retaining in their country the money which otherwise would have to be sent abroad to purchase pig iron in the crude and manufactured state.

Sixth—The development of steel plants and rolling mills using only electric energy.

ESTIMATE FOR A 10,000 HORSE-POWER PLANT[1] PRODUCING 120 TONS OF PIG IRON PER DAY OF TWENTY-FOUR HOURS.

Furnaces, contacts, overhead work	$ 24,500
Bins, chutes, elevators	14,000
Crushers	4,000
Hoists and regulators	10,500
Instruments	1,400
Cables for conductors	8,400
Building	10,500
Mixer and casting machine	10,000
Traveling crane and tracks	5,000
Ladles	1,500
Slag trucks	3,000
Ore bins	3,000
Repair shop	5,000
	$100,800
Charcoal plant	50,000
Power plant (assuming cost of developing one electric horse-power = $50.00)	500,000
	$650,800
Electrode plant	6,000
Unforeseen expenditure	43,200
	$700,000
Amortization: 5 per cent. Depreciation: 5 " " Interest: 5 " " } 15 per cent. on $700,000	105,000
On a production of 43,200 tons per year of 360 days per ton of pig iron	$ 2.43

COST OF PRODUCTION PER TON PIG IRON.

Ore (55 per cent. metallic iron) at $1.50 per ton	$ 2.70
Charcoal, one-half ton at $6.00 per ton	3.00
Electric energy, amortization, etc	2.43
Labor	1.00
Limestone	0.20
Eighteen lbs. of electrode at 2 cents per lb	0.36
General expenses	1.00
Total	$ 10.69

The figures here given on the authority of Dr. Héroult are outside figures and I desire to make the following remarks respecting them:

[1] This estimate is given on the authority of Dr. P. Héroult.

First—The price of ore will depend upon its quality and on local conditions and is not, therefore, a fixed figure.

Second—As stated previously, many water-powers in Ontario and Quebec can be developed to furnish an electirc horse-power year at from $4.00 to $5.00. This lower cost will reduce the electric energy required per ton of pig, as stated in the estimated cost.

Third—A better class of charcoal than was available for the experiments and proper protection against its consumption on top of the furnace will materially decrease the quantity of charcoal required per ton of pig, as stated in the cost sheet, and consequently lower the cost of production below the figures stated.

DEPARTMENT OF MINES,
OTTAWA, CANADA.

FORMALDEHYDE DISINFECTION. DETERMINATION OF THE YIELD OF FORMALDEHYDE IN VARIOUS METHODS OF LIBERATING THE GAS FOR THE DISINFECTION OF ROOMS.[1]

BY DANIEL BASE.

Received June 9, 1906.

IN the multitude of experiments on disinfection by formaldehyde gas very few of the experimenters have made any attempt to determine the exact amount of formaldehyde gas that entered the room from the charging apparatus. Several writers make reference to the percentage of the gas present in the air of the room, but they either do not state how the determinations were made or they obtain the percentage indirectly;[2] M. von Brunn,[3]

[1] These experiments were performed in the Division of Pharmacology, Hygienic Laboratory, U. S. Public Health and Marine Hospital Service, and are published by the permission of Surgeon-General Wyman; the results are incorporated in Bulletin 27, of the Hygienic Laboratory, where they are used by Dr. T. B. McClintic to illustrate his bacteriological results.

[2] Kinyoun: "Formaldehyde as a Disinfecting Agent and its Practical Application," Pub. Health Rep., U. S. P. H. & M. H. S., Jan. 29, 1897; Sprague: "Rapid Disinfection with High Percentages of Formaldehyde," Medical News, Dec. 11, 1897 (work done in the Hyg. Lab., U. S. P. H. & M. H. S.); Hill and Rickards: "Notes on Formaldehyde," Proc. 13th Ann. Meeting, Am. Pub. Health Assn., Dec. 9–12, 1902 (work done in Boston Board of Health Bacteriological Laboratory).

[3] v. Brunn: "Formaldehyddesinfection durch Verdampfung verdünnten Formalins" (Breslauer Methode), Z. Hygiene und Infectionskrankheiten, 30, 201 (1899).

however, made determinations directly on the charged air of a room by drawing 20 liter volumes of the air through water and titrating the formaldehyde absorbed by the iodine method. In those cases where the percentage of formaldehyde in the air of the room has been referred to, it was in connection with the particular method of charging with which the experimenter happened to be working. In my experiments the attempt has been made to determine the amount of formaldehyde gas given off into a room from a definite volume of formalin by five different methods, and from the results, to fix the relative standing of these methods as to the yield of formaldehyde gas.

These experiments were suggested by the publication of a new method of liberating formaldehyde gas from formalin, proposed in 1904 by Henry D. Evans, chemist, and Dr. J. P. Russell, bacteriologist, of the Laboratory of Hygiene, Augusta, Me.[1] The method consists in pouring the formalin quickly upon fine crystals of potassium permanganate, contained in a suitable metallic vessel. It was tested by Russell on over fifteen hundred cultures of bacteria exposed in different parts of rooms of various locations and dimensions. The results indicate this method of liberating the gas to be an efficient one, and if the same results be found by others, this method no doubt will supplant some of the older and more cumbersome methods, because of its ideal simplicity, the rapidity with which a room can be charged, and the inexpensive apparatus required. The Evans-Russell method seems an anomalous one as the formaldehyde gas is obtained by a process which destroys a part of the substance, and it was thought to be desirable to determine how much of the gas is given off in a room from a definite volume of formalin. For the sake of making a comparative study, other methods of charging a room were tried and determinations of the yield of formaldehyde made. The following methods were tried: the autoclave, Trenner-Lee retort, Kühn lamp, and the "sheet-spraying method."

Evans, in the article cited above, states that "all determinations of the amounts of formaldehyde were made by Romijn's potassium cyanide method,[2] as experience showed that this method is capable of yielding better results than the iodine

[1] "Formaldehyde Disinfection," 13th Ann. Rep., State Board of Health of Maine.

[2] Z. anal. Chem. 36, 18 (1897); Smith: This Journal, 25, 1028 (1903).

methods." The method of experimenting is not described. In a letter received after my experiments were under way, Evans states that he "is at present engaged with the analysis of the gas in closed rooms, drawing measured portions of the air through cyanide and iodine solutions." It would seem from this that he had not obtained the percentage yield which he claimed for his method of liberating formaldehyde gas from formalin by examination of the air in a room. In my experiments the high yield which Evans gives in his article, namely, about 80 per cent., was by no means obtained.

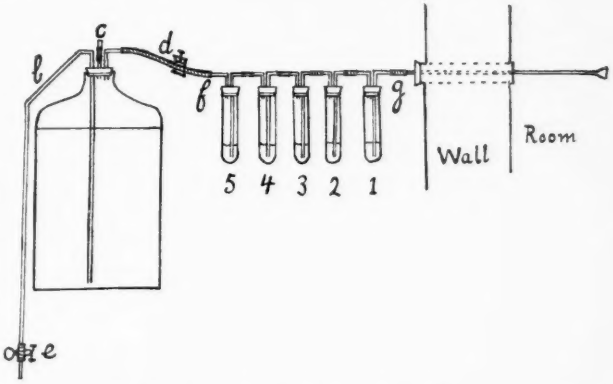
DESCRIPTION OF APPARATUS AND METHOD OF PROCEDURE.

The room into which the gas was liberated contained 2,000 cubic feet of space and was lined on the sides and ceiling as well as on the floor with sheet zinc, which overlapped the frames of the windows and doors. There were two well-fitting windows on opposite sides and two doors on the other two opposite sides. One of the doors had a small pane of glass inserted into it through which a view into the room was possible at all times. The wall containing this door was pierced by three parallel rows of zinc tubes about two inches in diameter and closed by rubber stoppers. The joints between the inner ends of the tubes and the wall of the room were made air-tight. The tubes of the middle row, which were about midway between the floor and ceiling and about six feet from the former, were used for drawing air from the room. For this purpose an ordinary glass tube about three feet long, to the end of which a small funnel was fitted, was passed through the rubber stopper and allowed to project outside the room about three inches. This end was joined by a rubber connection with a series of five thick-walled test-tubes about $7 \times {}^{3}/_{4}$ inches, fitted with alternating long and short connecting glass tubes. The lower end of each long tube was tapered to a small orifice. For purposes of reference we may call these tubes 1, 2, 3, 4 and 5, tube 1 being next to the room.

The tubes contained the absorbing medium through which the air of the room was drawn by means of a partial vacuum. A large graduated bottle holding 20 liters of water, fitted with an inlet tube, a siphon tube, and an air tube was used for this purpose. The whole arrangement is shown in the figure below.

When everything was ready connection was made at *g* and *f*,

the screw-cock *d* was closed, the siphon *b* started by opening the pinch-cock *e*, and water allowed to flow until the level in the bottle was exactly on the upper line of the graduation, at which moment the cock *e* was closed; then the glass plug *c* was inserted.



The apparatus was now ready for starting the experiment. It is needless to say that the bottle, with all its tubes, up to the point *d* was tested for leaks. All rubber joints were tied before the experiment was started and tight-fitting rubber stoppers were used in tubes 1, 2, 3, 4 and 5.

To begin the experiment cock *e* was opened, whereby water flowed out until a certain partial vacuum was reached in the bottle, when it ceased. Then *d* was opened cautiously and the rate of bubbling of the air from the room through the tubes 1, 2, 3, 4, and 5 was so regulated that 10 liters of air required about one hour and fifteen minutes; this rate is easily secured after a few trials. As soon as the air began to bubble, the water started to run again from the siphon tube *e*. The flow was continued until the level in the bottle had reached the desired mark of the graduation, when cock *e* was closed. Air continued to bubble until the partial vacuum in the bottle was reduced.

In order to make the conditions of pressure as nearly as possible like those in the apparatus at the beginning, the long tubes in 1, 2, 3, 4, and 5 were drawn up until the orifices were just below the surface of the liquid. This caused more air to bubble through the tubes. The volume of air drawn from the room is measured by

the volume of water that flowed from the bottle between the two marks of graduation. Finally tube 1 was disconnected at *g* and tube 5 at *f*. The series of tubes was then removed for titration.

SOLUTIONS AND TITRATION.

As the quantity of formaldehyde in a relatively small proportion of the air (say 10 liters) of the room was small, it was decided to use the potassium cyanide method of titration and also to use a solution of potassium cyanide as absorbing medium. The cyanide method is admitted to be accurate for small quantities of the aldehyde.

Potassium Cyanide Solution.—This was made by dissolving 3.3 grams of the salt (purity of 96 per cent. or over) in water; the volume was made up to 500 cc. The solution was standardized in the usual way against an excess of a decinormal solution of silver nitrate acidified with 4 or 5 drops of concentrated nitric acid, the excess of silver solution in the filtrate being determined by a standard sulphocyanate solution with iron alum as indicator.

In the titration of a dilute formaldehyde solution a definite volume or weight (known not to be in excess) is added to 10 cc., or more if necessary, of the standard potassium cyanide solution. The latter, after stirring, is added to an acidified excess of decinormal silver nitrate solution, the whole made up to 100 cc. or 200 cc., and the excess of silver in 50 or 100 cc. of the clear filtrate titrated with sulphocyanate. From the amount of sulphocyanate required the volume of silver nitrate precipitated by potassium cyanide is calculated, and the difference between this and the volume of silver nitrate equivalent to the amount of cyanide solution originally taken is the number of cubic centimeters of silver solution that represents the formaldehyde present; this number of cubic centimeters multiplied by 0.003 (more correctly 0.00298) gives the weight of absolute formaldehyde, HCOH.

The silver cyanide precipitate must be removed before titrating an excess of silver by sulphocyanate, because it interferes with the sharpness of the end-point and causes error.

As stated in the foregoing, potassium cyanide solution was chosen as the medium for absorbing the formaldehyde gas in the air of the charged room. It was soon discovered that the air bubbling through the solution carried away a little hydrocyanic acid. To avoid loss of the latter the last tube containing the

cyanide solution was followed by one containing silver nitrate solution, which effectually precipitated all the hydrocyanic acid carried over into it. The silver nitrate tube was followed by one containing distilled water. This tube showed no trace of hydrocyanic acid when tested by the ferric ferrocyanide reaction, and no formaldehyde when tested by Schiff's fuchsin-bisulphite reagent,[1] or ammonio-silver nitrate solution.

In preliminary experiments the contents of the silver nitrate tube, after formaldehyde-laden air had been drawn through the series, was tested for formaldehyde to determine if any had escaped absorption in the cyanide tubes. To some of the liquid, about 2 cc. of Schiff's reagent were added; a precipitate of silver chloride was produced, but no pink or purple color, thus indicating the absence of formaldehyde. For comparison the reagent was also added to a few cubic centimeters of silver nitrate solution to which had been added a trace of formaldehyde; the contents of the tube soon acquired a pink color. It seemed evident that formaldehyde is wholly absorbed from air passing through a series of tubes containing cyanide solution. This conclusion was further strengthened by experiments on the absorption of formaldehyde from air by water alone.

After nearly all the results given further on had been obtained by the cyanide method, there came to my notice an article by Trillat[2] in which the author states that formaldehyde can be completely absorbed from air by passing it through a sufficient number of absorption tubes containing water alone. This suggestion was put to the test and it was found that three water tubes absorbed all of the formaldehyde, the last tube containing only a trace. My reason for not having chosen water at the start as an absorbing medium was that I supposed a solution containing a substance, as cyanide, which combines chemically with formaldehyde would be better suited than pure water as an absorbing agent. Owing to circumstances, it was not possible for me to repeat all of the experiments and use water tubes to absorb the formaldehyde, but in several instances the absorption

[1] Schiff's reagent: This is prepared by adding 20 cc. of a solution of sodium bisulphite (sp. gr. 1.27) to 1000 cc. of aqueous fuchsin solution (1:1000), and, after one hour, adding 10 cc. of pure concentrated hydrochloric acid. It should be preserved in a well stoppered bottle.

[2] Trillat, A.: "Présence normal de la formaldéhyde dans les produits de la combustion incomplete," Rev. Hyg., Vol. 27, No. 2, Feb. 20, 1905.

from the same charged air of the room was carried out in cyanide tubes and in water tubes, side by side. Although three tubes are sufficient, five tubes of water were used for greater certainty. In these parallel experiments the percentage results in the case of absorption by water were practically the same as those in the case of absorption by cyanide. On examining the literature before putting my results together, I found von Brunn's article, in which he determined formaldehyde by drawing the charged air through water. von Brunn used in his determinations 3 Drechsel gas wash-bottles, each containing 100 cc. of water and aspirated 20 liters of air in twenty to thirty minutes. This would have been a too rapid rate for the volumes of liquid used in the absorbing tubes in my experiments, in which the rate of aspiration was from one-fourth to one-fifth as fast as in von Brunn's experiments. He found that nearly all of the formaldehyde was absorbed in the first bottle, the third one containing practically none.

DETAILS AS TO QUANTITY AND MANIPULATION IN THE DETERMINATION OF FORMALDEHYDE IN THE AIR OF THE CHARGED ROOM.

To give the figures involved in obtaining each result tabulated below would needlessly increase the length of this paper, but to give an idea of quantities of reagents used and method of carrying out the titration one experiment will be described in full.

Tube 1 contained about 8 cc. KCN solution.

Tube 2 contained about 5 cc. KCN solution.

Tube 3 contained 2 cc. KCN solution.

Tube 4 contained about 8 cc. N/10 $AgNO_3$ solution.

Tube 5 contained about 10 cc. distilled water.

Only the total quantity of cyanide need be measured, which, in this case, was exactly 15 cc., distributed about as stated. There should be not less than 8 or 9 cc. of cyanide solution in the first tube, lest there be an excess of uncombined formaldehyde in the liquid at the end of the absorption. Distilled water was added to the three cyanide tubes to make the column of liquid about 1.5 inches high, and to the silver nitrate tube to make a column about 1 inch high. The tubes were connected and air drawn through them as described above.

Volume of air drawn from room was 10 liters.

Time required to draw air was one hour, four minutes.

The five tubes were disconnected. Seven cc. of N/10 $AgNO_3$ solution were introduced into a 250 cc. flask and 8 or 10 drops of strong nitric acid added, then through a funnel, the silver nitrate solution in tube 4 and its connecting tubes was carefully rinsed into the flask, followed in like manner by tubes 1, 2 and 3. The flask was then filled to the graduation mark with water and the contents thoroughly shaken. One hundred cc. of the clear filtrate were titrated for excess of silver nitrate; 1.4 cc. of potassium sulphocyanate solution were required.

Ten cc. KCNS solution = 10.21 cc. N/10 $AgNO_3$.

Ten cc. KCN solution = 9.64 cc. N/10 $AgNO_3$.

By calculation the formaldehyde absorbed from the 10 liters of air corresponded to 3.03 cc. N/10 silver nitrate solution, which represents $3.03 \times 0.003 = 0.00909$ gram of formaldehyde. One cubic foot of the air (28.315 liters) contained 0.0257 gram of formaldehyde.

The quantity of formalin used to charge the room in nearly all the experiments, tabulated further on, was 600 cc. of 35.66 per cent. by volume; *i. e.*, 100 cc. of the formalin contained 35.66 grams of absolute formaldehyde. The strength was determined by the Blank and Finkenbeiner method of titration with hydrogen dioxide and caustic soda solutions.[1] The formalin was taken from the same supply in all the experiments.

In the experiment just described 600 cc. of formalin were used to charge the room. The results may be expressed in percentage, based on the amount of absolute formaldehyde taken per cubic foot of space in charging the room. The weight per cubic foot is

$$\frac{600 \text{ cc.} \times 0.3566}{2000} = 0.107 \text{ gram HCOH.}$$

The percentage would be $\frac{0.0257 \times 100}{0.107} = 24.01$.

From von Brunn's determinations, the question would seem to arise whether in my experiments the amount of formaldehyde found in the air of the room really represented all the formaldehyde in the room. To make this clear, it will be necessary to state the results of von Brunn's experiments. He first showed that when diluted solutions of formaldehyde are distilled from flasks, no paraformaldehyde is formed in the distillate or the

[1] For description, see original article in Ber. 31, 2979, or the U. S. Pharmacopoeia, 8th decennial revision, or Sutton's "Volumetric Analysis."

residue, as far as could be judged by the absence of cloudiness in the liquids when cooled, and that the sum of the amounts of formaldehyde found in the distillate and residue was practically equal to the amount of formaldehyde present before distillation. The concentrations of the solutions distilled ranged from 21.5 to 4.35 per cent. He states that paraformaldehyde is formed only when the concentration of a solution rises above 40 per cent. during distillation, but that with diluted solutions, for example 20 per cent. or less, there is little tendency for the per cent. to rise in the residue in the flask during distillation.

von Brunn next proceeded to make distillations from the "Breslau still" devised by C. Flügge,[1] of Breslau. This still has a large heating surface and relatively small outlet so that the pressure rises to 29 cm. of water (about 2.1 cm. of mercury). In two distillations of diluted formalin and determination of the formaldehyde in the distillate and residue, there was a loss of about 2 per cent., which was accounted for by the collection of some paraformaldehyde in the tube of the condenser. When this was titrated, it made up the difference. von Brunn attributed the formation of the small quantity of paraformaldehyde to the increase of pressure in the Breslau still as compared with that in the case of distillation from glass flasks.

Having thus a means of knowing pretty closely how much formaldehyde entered a room by determining how much remained in the residue in the still, von Brunn determined the amount of formaldehyde in the air of a charged room, in the manner already stated. He made three determinations, and the highest amount obtained was 16.94 per cent. of the total weight of formaldehyde introduced into the room. He worked with approximately 8 per cent. solutions, and in the experiment just mentioned, 2990 cc. of liquid, containing 255.6 grams of formaldehyde, were evaporated into a room of 2824 cubic feet. A piece of filter-paper hung up in the room and removed half an hour after the charging was finished, was found to have absorbed formaldehyde at the rate of 1.236 grams per square meter of surface. The conclusions at which von Brunn arrived may be interesting to some who are concerned with disinfection by formaldehyde and they are therefore given here. "It can be said

[1] Flügge: "Die Wohnungsdesinfection durch Formaldehyd," Z. Hyg. und Infectionskrankheiten, **29**, 276 (1898).

that the greatest portion of the liberated formaldehyde is condensed at once on the surface of the walls and on the objects in the room. Accordingly the idea that in disinfection the formaldehyde acts as a gas needs correction. The more experiments have been made with formaldehyde, the more has it been observed that its maximum germicidal effect can only be attained in the presence of an abundance of water vapor. Therefore it appears that, by vaporizing formaldehyde, we only accomplish a uniform distribution of the disinfectant in space, but that the real efficacy lies not in the formaldehyde gas, but in the solution which condenses everywhere on surfaces."

von Brunn and all others who used the Breslau method of Flügge to charge rooms made it a point to bring the moisture up to or very nearly to the saturation point, under which conditions formaldehyde will no doubt be condensed upon objects ordinarily present in rooms much more readily than when the moisture is short of saturation. In my experiments the air of the room became saturated with moisture in only one case, namely, in charging with the Kühn alcohol lamp; moreover, there were no objects in the room and the only surfaces exposed to the formaldehyde gas that were not zinc-lined, were those of the glass windows and their frames. It is not probable that any considerable amount of formaldehyde was condensed on the zinc walls of the room. In fact there is good reason for believing that there was practically no condensation, because determinations made on the total amount of formaldehyde charged into a large glass bottle (24 liters) by the permanganate-formalin method on a reduced scale, agreed fairly well with those made on the air of the large room charged by the same method. Had there been such loss of formaldehyde from the air of the room by condensation upon the walls as von Brunn states, the results just referred to would never have approximated as closely as they did. The results of the determinations of the formaldehyde charged into the glass bottle are given in Tables 6 and 7.

Von Brunn did not state what the conditions were in the room which he charged, but it is probable that it was an ordinary one and contained the objects usually present, such as chairs, table, clothing, etc. In fact most experimenters have purposely left such objects in rooms in order to have conditions very nearly like those in living rooms when about to be disinfected.

Axel Jörgensen[1] found that paper, cloth, etc., condense formaldehyde from moist air laden with it, and that a room with wooden walls, having been charged and then ventilated for several days until the odor had vanished and closed again for more than a month, had developed such an odor of formaldehyde when opened that one could not endure remaining in it. He concludes that the total surface of walls in rooms is important, and that proportionately more formaldehyde should be introduced when there is a large wall-surface to compensate for the greater condensation and thus leave the same amount of gas in the air as would be present in a smaller room with less condensation. This point has also been brought out by Peerenboom, Walter and Schlossmann, and Werner. Jörgensen recommends for disinfection purposes rooms with walls of stone, glass, or metal.

If von Brunn's experiments were made in an ordinary room with objects in it and walls of absorbing material, the small percentage of the total formaldehyde introduced that he found in the air of the room can readily be accounted for. In my experiments it seems quite certain for the reasons given above that the amount of formaldehyde found in the air actually represented the whole amount of formaldehyde in the room at the time, or in other words condensation of formaldehyde upon the zinc walls did not occur.

As already stated, the windows and doors of the room into which the charges of formaldehyde were introduced, were tight-fitting, more so than those of the average living room, yet the room was not perfectly air-tight. Therefore the results recorded further on do not represent the total amount of formaldehyde that left the charging apparatus, but rather the average amount present in the room during the time of the determination and after a certain interval from the time the charging was finished. On a quiet day the rate of leakage was relatively small as is shown by the results, so that the amount of formaldehyde found on such a day soon after the charge was introduced must be fairly close to what would have been found if the room had been perfectly air-tight. In a few experiments, the window-frames and cracks of the doors

[1] Jörgensen: "Untersuchungen über Formaldehyddesinfection nach der Breslauer Methode,—speciell Desinfection von Uniformen betreffend," Z. Hygiene und Infectionskrankheiten, **45**, 237 (1903).

were covered by pasting on heavy smooth paper, but the amount of formaldehyde found was only a little larger than when the paper was omitted; this would seem to show that the rate of leakage from the room was small.

PERMANGANATE-FORMALIN METHOD OF CHARGING THE ROOM, PROPOSED BY EVANS AND RUSSELL.

When formalin is poured upon crystals of potassium permanganate a vigorous action takes place after a few seconds, accompanied by a strong ebullition of the liquid and sufficient heat to produce a large quantity of steam. The reaction is apparently over in a comparatively short time (about five minutes) and with proper proportion of substances, the residue in the vessel is almost dry. The heat produced by the action of the permanganate on a portion of the formaldehyde is sufficient to evaporate nearly all the remainder.

The exact nature of the chemical reaction that takes place was not investigated as for the purposes of the experiments the fact of main interest was that an abundance of formaldehyde is given off in gaseous form. According to Evans and Russell, "analysis of the gas thrown out into a room by this reaction showed it to consist of formaldehyde, water vapor, carbon dioxide, and a very small amount of formic acid. In the generator were found a lower oxide of manganese, a little formaldehyde, carbon dioxide, potassium hydroxide, and, I think, a little potassium formate resulting from the neutralization of the potassium hydroxide by formic acid." It seems highly probable that the decomposition takes place essentially according to the following reaction:

$$4KMnO_4 + 3HCOH + H_2O = 4MnO(OH)_2 + 2K_2CO_3 + CO_2.$$

In accordance with this reaction about one-fifth of the formaldehyde is destroyed. The reaction is of value, of course, only because it furnishes the heat necessary to vaporize the rest of the formaldehyde.

Evans and Russell used the ratio of 100 cc. of formalin to 37.5 grams of permanganate, but it was found in the present experiments that with this proportion considerable formalin remained in the residue in the generator, as was evidenced by its wet condition and powerful odor of formaldehyde. After some experimenting the ratio of 100 cc. of formalin to 50 grams of permanganate was adopted; this gave a residue fairly free from liquid.

The quantity used to charge the room of 2,000 cubic feet was in nearly all cases 600 cc. formalin (35.66 per cent. by volume). The generator was a galvanized iron pail 10 inches wide and 10 inches high holding 12 liters (3 gallons). The ebullition was so vigorous that the frothy mass often reached nearly to the top of the pail. The pail was placed in the center of the room, the permanganate dropped into it, the formalin poured quickly upon it, and a hasty exit made from the room.

The action is more rapid, the more finely powdered are the permanganate crystals; in the experiments to follow, the small needle crystals of commerce were used without further powdering.

Many variations of conditions might have been tried, such as covering the pail with sheet asbestos to retain the heat, or heating the pail before the experiment, or placing it in hot water, or powdering the permanganate crystals, etc., but as time was a factor it was thought best to adopt those conditions which would be least cumbersome to execute by public officers or others in disinfecting rooms.

In the experiments (Table I) the ratio of the quantities used was 100 parts by volume of formalin to 50 parts by weight of permanganate, and approximately fifteen minutes were allowed to elapse between the time of mixing these and the beginning of drawing the air through the absorption tubes. This seemed sufficient time for the action to cease and for the formaldehyde gas to diffuse through the air of the room. The relative humidity in the room before and after charging was determined by means of a dry and wet bulb thermometer, which was so arranged that it could be swung around in the room and the results observed by the operator through a pane of glass in the door. By means of tables the grains of moisture per cubic foot were calculated. Before a new charge was put into the room all formaldehyde of the previous one was gotten rid of by opening the door and windows until no odor was perceptible.

Comments.—Although the room in which the experiments were made was zinc-lined and the doors and windows were fairly close-fitting, yet it was not air-tight, so that the conditions were not of that exact quantitative character which obtains in an operation like the precipitation of sulphuric acid by barium chloride. In view of this fact, although the percentages vary by several units, they can be considered as agreeing fairly well. In III, where the

TABLE I.—EXPERIMENTS WITH PERMANGANATE AND UNDILUTED FORMALIN.

Date and temperature of room before experiment	Formalin (35.66 per cent. by volume). cc.	$KMnO_4$. Grams.	Time between mixing and drawing air.	Time required to draw air.	Volume of air drawn in liters.	Relative humidity before experiment.	Relative humidity ten minutes after mixing.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot.	Yield. Per cent.	Condition of wind, etc.
I. 6/27, '05, 71° F.	600	300	*a.* 14 min.	1 hr. 10 min.	10	72	86	1.47	0.107	0.0403	37.73	Moderate wind.
			b. 3 hrs. 38 min.	1 hr. 21 min.	10				0.107	0.0243	22.70	Moderate wind.
II. 6/28, '05. 69° F.	800	400	*a.* 12 min.	1 hr. 32 min.	10	63	86	2.0	0.1426	0.0505	35.41	Slight breeze.
			b. 22 hrs. 17 min.	1 hr. 10 min.	11				0.1426	0.0172	12.07	Very slight breeze.
III. 6/30, '05. 77° F.	400	200	15 min.	1 hr. 12 min.	10	79	85	0.58	0.0713	0.025	35 06	Moderate wind.
IV. 7/24, '05. 79° F.	600	300	17 min.	1 hr. 21 min.	10	79	94	1.72	0.107	0.0419	39.15	Practically no wind. Windows and doors of room pasted up.

room was made more nearly air-tight by pasting paper over the cracks of the door and covering the window frames, the per cent. is a little higher. These experiments also indicate that the relation between the formalin and permanganate in the ratio taken is fairly quantitative and that the percentage yield of formaldehyde gas is approximately the same whether 400, 600 or 800 cc. be taken for a charge. Experiments I *b* and II *b* give an idea of the rate of leakage of formaldehyde from the room. In I *b*, the loss after an interval of about three and one-half hours was 2/5 of the formaldehyde, in II *b* it was about 3/5 after an interval of twenty-two hours.

It is probable that on a very quiet day after fifteen or twenty minutes with a charge of 600 cc. formalin (35.66 per cent. by volume) the weight of the gas in the room would be at least between 38 and 39 per cent. of the weight in the 600 cc. of formalin taken, and in a room with fairly tight windows and doors.

EXPERIMENTS WITH PERMANGANATE AND DILUTED FORMALIN.

A number of experiments were made with formalin diluted with various quantities of water, and with different weights of permanganate.

A fixed volume of formalin was taken (600 cc.) and the interval between setting off the charge and beginning to draw air, the volume of air drawn (10 liters), and the time required to draw it were about the same as in Table I. In several instances two experiments were made simultaneously with 5 and 10 liters of air respectively.

Comments.—Of the various proportions used that of 600 cc. formalin, 300 cc. water and 375 grams of permanganate gives the highest yield of formaldehyde gas.

In Experiment I the determinations *a* and *b*, made simultaneously and on the same volume of air, gave the same results, which would seem to indicate that the method of analysis, under the same conditions, gives constant results. In Experiment III, 5 liters of air in *a* were drawn in the same time as 10 liters in *b* with practically the same result, which seems to point to the conclusion that 5 liters of air is a large enough quantity for a determination.

In Experiments IV, V, VI and VII the same proportion of materials were used to charge the room, but the results in IV are

TABLE II.—EXPERIMENTS WITH PERMANGANATE AND DILUTED FORMALIN.

	Date and temperature of room before experiment.	Formalin (35.66 per cent. by volume). cc.	Water. cc.	$KMnO_4$. Grams.	Time between mixing and drawing air.	Time required to draw air.	Volume air drawn in liters.	Relative humidity before experiment.	Relative humidity ten minutes after mixing.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot.	Yield. Per cent.	Condition of wind, etc.
I.	7/3, '05. 81° F.	600	600	450	17 min.	*a.* 1 hr. 20 min.	10	81	94	1.79	0.107	0.0272	25.4	Slight breeze.
						b. 1 hr. 20 min.	10				0.107	0.0272	25.4	Slight breeze.
II.	7/10, '05. 81° F.	600	300	450	16 min.	1 hr. 5 min.	10	83	98	2.06	0.107	0.03081	28.8	Moderate wind.
III.	7/11, '05. 81.5° F.	600	300	300	16 min.	*a.* 1 hr. 9 min.	5	74	94	2.28	0.107	0.0242	22.6	Moderate wind.
						b. 1 hr. 8 min.	10				0.107	0.02336	21.8	Moderate wind.
IV.	7/12, '05. 81° F.	600	300	375	14 min.	*a.* 45 min.	5	77	96	2.14	0.107	0.0289	27.0	Brisk wind.
						b. 1 hr. 14 min.	10				0.107	0.02965	27.7	Brisk wind.
V.	7/17, '05. 85° F.	600	300	375	15 min.	*a.* 34 min.	5	70	90	2.55	0.107	0.03755	35.1	Gentle breeze.
						b. 1 hr. 5 min.	10				0.107	0.0356	33.27	Gentle breeze.
VI.	7/18, '05. 85° F.	600	300	375	*a.* 17 min.	42 min.	5	70	88	2.3	0.107	0.0341	31.84	Gentle breeze.
					b. 17 min.	1 hr. 20 min.	10				0.107	0.03296	30.80	Gentle breeze.
					c. 2 hrs. 27 min.	1 hr. 18 min.	10				0.107	0.02548	23.81	Gentle breeze.
	Cont'd 7/19, '05.				*d.* 4 hrs. 24 min.	1 hr.	10				0.107	0.02276	21.27	Gentle breeze.
					e. 24 hrs. 33 min.	1 hr. 23 min.	10				0.107	0.01028	9.6	Gentle breeze.
VII.	7/21, '05. 79° F.	600	300	375	*a.* 21 min.	47 min.	5	79	94	1.72	0.107	0.03517	32.87	Practically no wind;
					b. 21 min.	1 hr. 17 min.	10				0.107	0.03517	32.87	windows and doors
	Cont'd 7/22, '05.				*c.* 4 hrs. 7 min.	1 hr. 18 min.	10				0.107	0.02658	24.84	pasted up with
					d. 23 hrs. 46 min.	1 hr. 13 min.	10				0.107	0.01546	14.44	stout smooth paper.

low on account of the brisk wind blowing at the time, and should not be compared with those of V, VI and VII. The three determinations of V, VI and VII which are comparable show a fairly close agreement. VI and VII show the rate of leakage from the room, the loss of formaldehyde in VI in two, four and twenty-four hours after the first determination being about 2/10, 3/10 and 7/10 respectively, in VII after four and twenty-three and one-half hours being about 25/100 and 56/100 respectively, *d* and *e* of VI and *c* and *d* of VII, which are comparable, show that when there is very little wind the leakage from the room when pasted up with paper is not much less than when it is not pasted. V *a* seems to be abnormally high when compared with VI *a* and VII *a*.

With the proportions of 600 cc. formalin (35.66 per cent.), 300 cc. water and 375 grams potassium permanganate, it is probable from the results that after fifteen or twenty minutes on a quiet day in a tight room the amount of formaldehyde gas obtained would be approximately 32 per cent.

The addition of water to the formalin has the effect of increasing the amount of moisture sent out into the room which probably would offset in disinfection the lower per cent. of formaldehyde obtained than in the case of undiluted formalin, since it is claimed by many that high relative humidity is an important factor in the action of formaldehyde gas upon bacteria.

CHARGING THE ROOM BY THE AUTOCLAVE.

Six hundred cc. of formalin, 60 cc. of glycerol, 120 grams of calcium chloride, and water sufficient to make a volume of 1000 cc. constituted the charge for each experiment. The pressure was raised to between 50 and 60 pounds, when the cock was opened and injection continued till the pressure had fallen to about 20 pounds. Then the pressure was raised and vapor again injected.

This process was repeated until the pressure rose very slowly and vapor almost ceased to escape from the nozzle of the autoclave, which was inserted through a suitable hole in the door. After each experiment there was little liquid left in the autoclave.

Comments.—From the result of III *a* it seems probable that on a calm day in a fairly tight room the amount of formaldehyde by the autoclave from 600 cc. of formalin would be approximately 42 per cent. after an interval of about thirty minutes from the time of removing the nozzle from the room.

TABLE III.—EXPERIMENTS WITH THE AUTOCLAVE.

Date and temperature of room before experiment.	Time required to exhaust autoclave.	Time between beginning of discharge to drawing of air.	Time required to draw air.	Volume of air drawn in liters.	Relative humidity before experiment.	Relative humidity five minutes after removing autoclave.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot.	Yield. Per cent.	Condition of wind.
I. 6/23, '05. 80° F.	25 min.	3 hrs. 32 min.	1 hr. 18 min.	10	75	96	2.96	0.107	0.0406	37.94	Almost no wind.
II. 6/26, '05. 81.5° F.	25 min.	*a.* 35 min.	1 hr. 17 min.	10	81	94	2.00	0.107	0.04213	39.37	Good breeze.
		b. 3 hrs. 33 min.	1 hr. 4 min.	10				0.107	0.0216	20.18	Storm.
III. 7/15, '05. 80° F.	22 min.	*a.* 40 min.	1 hr. 10 min.	11	75	94	2.23	0.107	0.04448	41.57	Almost no wind.
		b. 1 hr. 41 min.	1 hr. 20 min.	11				0.107	0.04116	38.46	Almost no wind.

II *a* is lower than III *a*, which was to be expected because of the stronger wind blowing.

II *b* shows the rapid loss of formaldehyde gas during a strong wind or storm. During the time the air was drawn in this experiment a severe thunderstorm was in progress, with the result that during the interval of three hours between *a* and *b* nearly half the formaldehyde escaped from the room.

Apparently over half the formaldehyde gas in the 600 cc. of formalin used to charge the air was lost. It is altogether improbable that the most of this escaped from the room during the twenty-five minutes required to exhaust the autoclave, as is evident from the slow rate of loss on a calm day shown in I and III *a* and *b*. It is more probable that under the high temperature and pressure in the autoclave the formaldehyde undergoes change. It would be an interesting problem to work out the fate of the lost formaldehyde. The mixture of formalin, glycerol and calcium chloride was devised by A. Trillat to prevent, as he asserted, the formation of paraformaldehyde. If the results in my experiments represent the amount of formaldehyde injected into the room, and there seems to be no strong reason to think the contrary, then there is a loss of formaldehyde somehow in the autoclave. There are two plausible views, either that the formaldehyde is partly decomposed, or polymerized, or perhaps both.

CHARGING THE ROOM BY THE TRENNER-LEE RETORT.

The formalin in this method is simply heated to the boiling-point under atmospheric pressure in a retort and the issuing water vapor and formaldehyde gas are passed into the room through a suitable tube.

In the following experiments 600 cc. of formalin to which were added 6 cc. of glycerol were taken for the charge, and the heat was continued under the retort until vapor practically ceased to issue from the outlet tube. When the retort was removed there was little liquid left in it.

Comments.—The yield of formaldehyde gas by this method was appreciably higher than by the autoclave method, although the time required to exhaust the apparatus was more than twice as long in the former as in the latter. Because of this longer time there was naturally more loss by leakage in this method before beginning to draw air. The higher percentage would be ex-

TABLE IV.—EXPERIMENTS WITH TRENNER-LEE RETORT.

Date and temperature of room before experiment.	Time required to exhaust retort.	Time between removal of retort and drawing air.	Time required to draw air.	Volume of air drawn in liters.	Relative humidity before experiment.	Relative humidity at end of injection.	Increase in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot. Gram.	Yield. Per cent.	Condition of wind.
I. 7/27, '05. 73° F.	1 hr.	22 min.	1 hr. 6 min.	10	73	86	1.5	0.107	0.05037	47.07	Very slight breeze.
II. 7/28, '05. 76° F.	1 hr.	*a.* 21 min.	1 hr. 10 min.	10	82	89	0.96	0.107	0.04935	46.12	Very slight breeze.
Cont'd 7/31.		*b.* 3 hrs. 40 min.	1 hr. 4 min.	8				0.107	0.04183	39.1	Very slight breeze.
		c. 72 hrs.	1 hr. 7 min.	10				0.107	0.00637	5.95	Strong wind, July 29, 30, 31.

pected, since in the retort the formaldehyde is not subjected to as high a temperature and pressure as in the autoclave. Although the yield was greater in the retort method than in any other tried, there arises the question as to what becomes of the rest of the formaldehyde. In view of von Brunn's experiments, it seems probable that some of the formaldehyde was polymerized to paraformaldehyde the greater part of which perhaps remained in the retort. It is also likely that some paraformaldehyde entered the room, although there was nothing in the appearance of the room atmosphere to indicate this. The atmosphere was clear.

Experiments II *a* and *b* show the slow rate of leakage from the room on a quiet day, the loss in an interval of three hours and twenty minutes being about 3/20 of the amount found in *a*. I and II agree very closely, the difference being only about 1 per cent. From I and II, it seems probable that on a quiet day in a tight room the amount of formaldehyde gas present by this method after an interval of twenty minutes from removal of the retort would be approximately 47 per cent.

In regard to the question of the formation of paraformaldehyde when formalin is heated, most contradictory statements are found in the literature. Novy and Waite[1] assert the following: "The fear of polymerization of formalin on boiling is not well grounded. Certain it is that formalin can be distilled from its aqueous solution without polymerization, and that the results obtained are in every way equal to those obtained from paraform and decidedly superior to the so-called formalin lamps." "The statement is freely made that formaldehyde solutions cannot be heated without polymerization and thus interfering with further evaporation. Formalin, if heated slowly in an open dish, may possibly polymerize, especially when concentrated to about 25 cc., but we have never found this to take place when the formalin solution was rapidly heated in a glass flask or copper container." On the other hand von Brunn in the article cited, which was published a year later, stated that when formalin of about 32 per cent. or more was distilled from a glass flask, the residue in the flask upon cooling became cloudy or opaque, indicating paraformaldehyde. Only when diluted solutions, 20 per cent. or less, were distilled, was there no paraformaldehyde formed. Novy and Waite had used

[1] "The Disinfection of Rooms," Med. News, 72, 641 (1898).

an approximately 40 per cent. solution. The loss of formaldehyde as indicated in my determinations seems to point to the formation of paraformaldehyde in the retort and to the correctness of von Brunn's statements.

SHEET-SPRAYING METHOD.

Two sheets, about 8 x 5 feet were hung up in the room in a slanting position at an angle of about 45°. It was found advantageous to have them just damp to the touch when hung up, as the formalin was absorbed by the fibers more quickly and had very little tendency to run off the sheet. Six hundred cc. of formalin were sprayed uniformly and the door closed. About one and one-half hours were allowed for the formaldehyde to diffuse before beginning to draw air. The sheets were washed before the next spraying.

Comments.—Compared with the previous methods this one produces a fairly good quantity of formaldehyde gas in the air of the room. The results show that the quantity increases during a relatively long period of time. In Experiment II *c* the quantity of formaldehyde gas found after an interval of twenty-two hours was only 2.75 per cent. less than that found in II *a*, ninety minutes after closing the room.

Evidently, an advantage of this method is the fact that formaldehyde continues to be supplied to the air of the room for a long time, whereas, in the other methods, the per cent. of the gas begins to diminish by leakage from the moment the charging is finished.[1]

It is impossible to indicate the yield of gas in this method, as the gas is given off continuously for a long period. Moreover it is probable that on a dry day the amount of gas given off after a definite interval would be greater than on a very humid day, on account of slower evaporation in the latter case, and no doubt low temperatures would also have a retarding effect on the evaporation.

EXPERIMENT WITH THE KÜHN LAMP.

This is one of the various lamps devised for the purpose of generating formaldehyde by the partial oxidation of methyl

[1] The high degree of efficiency of this method, from the bacteriological side, has recently been emphasized by Ravenel and Gilliland, Univ. of Penn. Med. Bull. Vol. 16, p. 77.

TABLE V.—EXPERIMENTS WITH SHEET-SPRAYING METHOD.

Date and temperature of room before experiment.	Time between closing room and drawing air.	Time required to draw air.	Volume of air drawn in liters.	Relative humidity before experiment.	Relative humidity after closing room.	Gain in grains of moisture per cubic foot.	Absolute formaldehyde taken per cubic foot. Gram.	Absolute formaldehyde found per cubic foot.	Per cent.	Condition of wind.
I. 8/3, '05.	*a.* 1 hr. 26 min.	1 hr. 13 min.	10	72	83	1.6	0.107	0.02576	24.07	No wind.
76.5° F.	*b.* 3 hrs. 47 min.	1 hr. 8 min.	10		(after 5 hrs.)		0.107	0.03262	30.48	No wind.
II. 8/4, '05.	*a.* 1 hr. 40 min.	1 hr. 15 min.	10	83	85	0.49	0.107	0.0252	23.55	Gentle breeze.
78° F.	*b.* 4 hrs. 5 min.	1 hr. 7 min.	10		(after 3 hrs.)		0.107	0.0305	28.50	Gentle breeze.
Cont'd 8/5.	*c.* 23 hrs. 30 min.	1 hr. 17 min.	10				0.107	0.02225	20.80	No wind.

alcohol. In the Kühn lamp this is brought about by means of hot platinized asbestos, which has the power of causing the oxygen of the air and methyl alcohol vapor to combine according to the following reaction:

$$\underset{\text{methyl alcohol.}}{CH_4O} + O = \underset{\text{formaldehyde.}}{CH_2O} + H_2O.$$

The platinized asbestos is heated by first burning some of the alcohol, after which the flame is extinguished. Alcohol continues to vaporize and the heat produced in the oxidation keeps up the temperature of the apparatus. The time usually allowed for the exhaustion of the lamp is about two hours.

One thousand cc. of common methyl alcohol were placed in the reservoir of the lamp and 1500 cc. of water in the basin around the reservoir. During the action of the lamp an abundance of moisture was formed, which condensed on the small glass pane in the door of the room.

In a previous experiment it was found necessary to have two silver nitrate tubes to absorb the hydrocyanic acid which was carried over from the cyanide absorption tubes by the air bubbling through them. This was no doubt due to the presence of a great excess of carbonic acid and perhaps a small quantity of formic acid.

While formaldehyde is formed by the action of the platinized asbestos in the Kühn lamp it is not the only product of oxidation, for the oxidation extends as far as the formation of carbon dioxide. It is known that formic acid is oxidized to carbon dioxide by platinized asbestos. Engels condemns the methyl alcohol lamps and states that about 90 per cent. of the alcohol is oxidized to carbon dioxide and water and that the vapors from the lamps contain from 3 to 5 per cent. of carbon monoxide.[1]

The presence of either carbon dioxide or formic acid in the air bubbling through the cyanide absorption tubes would cause the liberation of some hydrocyanic acid, which would be carried over. The precipitate in the first silver nitrate tube was somewhat larger than in the case of the other methods. The precipitate in the second silver nitrate tube did not appear until towards the end of the experiment.

[1] Engels: "Experimentelle Beiträge zur Wohnungsdesinfection mit Formaldehyd," Archiv. Hygiene, 49, 129–199 (1904).

Result: Began to draw air two hours after the lamp was started. Volume of air drawn, 10 liters. Time required, one hour, thirteen minutes. Condition of wind, gentle breeze.

Temperature of room before experiment, 79; relative humidity, 87.

Temperature of room two hours after starting lamp, 85; relative humidity, 98.

If the quantity of formaldehyde found be referred for comparison to the amount of absolute formaldehyde allowed per cubic foot in the other methods, where 600 cc. of formalin were taken to charge the room, it is equivalent to $\frac{0.01096 \times 100}{0.107} = 10.24$ per cent.

Comments.—The quantity of absolute formaldehyde obtained from 1000 cc. of methyl alcohol is considerably less than that obtained from 600 cc. of formalin by any of the other methods. Because of this relatively small quantity and the cumbersomeness and unreliability of the lamp as a means of producing the gas it was not thought worth while to make further determinations. One merit which the Kühn lamp has is that it produces more moisture in the air of the room than the other methods described.

Conclusions.—The results obtained must be interpreted as representing the quantities of formaldehyde gas that may be expected to be present in a room made not absolutely but fairly air-tight when charged with formalin by the various methods described, on a day of little wind and after a certain interval of time which varies with the method used. According to the quantity of formaldehyde yielded it seems fair to arrange the methods in the following order:

(1) Trenner-Lee retort.

(2) Autoclave.

(3) Permanganate-formalin, 300 grams to 600 cc.

(4) Sheet spraying.

(5) Permanganate-diluted formalin in the proportions of 600 cc. formalin, 300 cc. water and 375 grams permanganate.

(6) Kühn lamp, using 1000 cc. methyl alcohol as against 600 cc. formalin in the other methods.

For simplicity and expedition, the permanganate-formalin method is preferable to all the others. Moreover, the quantity of formaldehyde gas can easily be increased by using more formalin, which only requires a larger pail, a piece of apparatus not very

difficult to obtain, and correspondingly more permanganate. If it is desirable or necessary to have a greater degree of humidity in the air than results from this method, that could easily be supplied from a simple tin or copper still.

Although the sheet spraying-method may not give at any time so high a percentage of the gas as the permanganate-diluted formalin method, it is placed before the latter, because in the spraying method the amount of gas is kept up for a long time, while in the diluted formalin method it is constantly diminishing and after five or six hours would be less than in the spraying method.

The experiments described were carried out at summer temperature, between 69° and 85° F. No attempt was made to determine if any solid paraformaldehyde was present along with the gaseous formaldehyde in the air of the room, but it is quite likely that none or very little was present, since the air of the room after charging was free from haziness.[1] Paraformaldehyde as such has no value as a disinfectant, but it has the same effect on potassium cyanide in titrations as the gaseous product.

It may not be out of place to add here the conclusions of a recent experimenter as to the "practical requirements for an effective formaldehyde disinfection."[2] (1) In all cases, an average of 5 grams of formaldehyde (absolute) per cubic meter of space (0.1416 gram per cubic foot) should be present, with seven hours' action. (2) In exceptional cases, where loss of formaldehyde can not be avoided, or where numerous objects or a good deal of matter of an organic nature which can not be

[1] M. B. Porch (assistant in Pharmacology, Hygienic Laboratory, Washington), using the same apparatus and methods that I did, but working at lower temperatures, found that polymerization of formaldehyde gas begins at about 62° F., and becomes more marked as the temperature decreases, which is evidenced by the persistent hazy condition of the air of the room, the low percentage yield of formaldehyde, and the deposition of paraformaldehyde in the room. He obtained in the permanganate-formalin method a yield of 25.1 per cent. at 62° F. and 11.1 per cent. at 52° F., as against 38.39 per cent. obtained by me at the higher temperatures of my experiments, namely, 71° and 79° F. He found similar results in the case of the autoclave method and that in the sheet-spraying method little formaldehyde is evaporated in cold weather and that polymerization takes place on the sheet.

[2] G. Werner: "Zur Kritik der Formaldehyddesinfektion," Archiv. Hygiene, 50, 305 (1904).

conveniently removed, are present in the room, the quantity of formaldehyde should be doubled. (3) In all cases, when the room temperature is below 50° F., it should be raised. 68–77° F. is an efficient temperature. (4) The strength of the formalin used should be known. Werner used the Breslau still in his experiments and saturated the air with moisture, using a hair hygrometer to determine the latter.

DETERMINATION OF FORMALDEHYDE CHARGED INTO A LARGE GLASS BOTTLE BY THE FORMALIN-PERMANGANATE METHOD, AND ALSO THE AMOUNT LEFT IN THE RESIDUE IN THE GENERATOR.

These experiments were carried out in two large bottles, one holding a trifle over 24 liters (0.85 cu. ft.), the other very nearly 18 liters (0.63 cu. ft.). The mouths of the bottles were 2.75 inches wide and were closed with tight-fitting corks, the pores of which were closed with melted paraffin.

A porcelain crucible holding 24 cc. was fitted into an excavated flat cork, which was suspended in a stirrup of thin twine.

The formalin was practically 40 per cent. by volume, as determined by the Blank and Finkenbeiner hydrogen dioxide method. In most of the experiments 0.7 cc. of this was used to charge the bottles; it was measured from a long slender pipette, in which 0.1 cc. made a column 1.7 cm. long. The method of procedure was as follows:

About 40 cc. of approximately decinormal potassium cyanide solution was measured from a burette into the bottle and about 50 cc. of water added. The liquid was then rolled over the side of the bottle to produce a greater absorbing surface. Then the crucible containing the formaldehyde was suspended in the mouth of the bottle, the permanganate dropped in from a piece of glazed paper, and the whole let down quickly into the bottle by a string and the cork securely placed. After a few seconds a vigorous action began, which seemed to be finished in about five minutes. About fifteen minutes, however, were allowed to elapse before the crucible was removed. This was done by slightly loosening the stopper, drawing up the crucible as near as possible to the stopper, removing the stopper for an instant, taking the crucible out, and then replacing the stopper. By repeatedly rolling the cyanide solution over the side of the bottle the formaldehyde was soon

absorbed (in about half an hour). When the odor of formaldehyde could no longer be detected, the contents of the bottle were transferred by thorough washing into a 500 cc. flask containing an excess of decinormal silver nitrate (about 10 cc.) acidified with nitric acid. The volume was made up to the graduation mark, the flask thoroughly shaken, and 250 cc. of the filtrate titrated with sulphocyanate solution, and calculation made as already described.

Method of procedure for the residue in the crucible. After the crucible was removed the contents were thoroughly extracted with water and filtered into a 250 cc. flask. The volume was made up to the graduation mark, and 50 cc. of the solution were added to about .5 cc. of the cyanide solution. After stirring, this was poured into an excess of acidified silver nitrate solution, which was stirred until the precipitate collected into a clot. The clear filtrate from the precipitate was then titrated with sulphocyanate solution for excess of silver.

Comments.—In all the experiments but the last two the ratio used was 1 part by volume of formalin to 0.5 part by weight of permanganate, the same as was used in the experiments of Table I. With this proportion the total amount of formaldehyde found in the air of the bottle and in the residue was fairly constant, considering the conditions of the experiments.

Evidently there is an advantage in using permanganate in powdered form, as is shown by comparing the results of IV, V, VI, VII and VIII with those of I, II and III. No doubt the reason for this is that action takes place more quickly with production of a higher temperature, so that more formalin evaporates from the crucible and less remains with the residue.

The results in Experiments I, II and III (average 33 per cent.) are lower than the results in Table I, which refer to experiments in charging the room of 2,000 cu. ft. This would be expected considering the small quantities used, whereby the quantity of heat produced is not so large, and the cooling of the generator is more rapid. In the experiments where powdered permanganate was used, the percentage yield is higher and in line with the results in Table I.

In Experiment IX, where only 0.5 cc. of formalin was used, the result is low; but this is probably due to the fact that the

TABLE VI.—RESULTS OF EXPERIMENTS IN GLASS BOTTLES.

	Date.	Size of bottle in liters	Formalin (40 per cent. by volume). cc.	$KMnO_4$. Gram.	Formaldehyde found in bottle. Per cent.	Formaldehyde found in residue. Per cent.	Total of formaldehyde found in bottle and residue. Per cent.	Remarks.
I.	8/15, '05.	24	1	0.5	33.03	.....	.....	$KMnO_4$ in small needle crystals.
II.	8/16	24	1	0.5	33.52	38.25	71.77	$KMnO_4$ in small needle crystals.
III.	8/18	18	1	0.5	32.47	40.35	72.82	$KMnO_4$ in small needle crystals.
IV.	8/17	18	0.7	0.35	35.48	33.86	69.34	$KMnO_4$ ground to moderately fine powder.
V.	8/18	18	0.7	0.35	36.53	35.20	71.73	$KMnO_4$ ground to moderately fine powder.
VI.	8/18	24	1	0.5	.....	35.11	.....	$KMnO_4$ ground to moderately fine powder.
VII.	8/21	18	0.7	0.35	37.00	32.20	69.20	$KMnO_4$ ground to moderately fine powder.
VIII.	8/22	18	0.7	0.35	37.83	32.76	70.59	$KMnO_4$ ground to moderately fine powder.
IX.	8/19	18	0.5	0.25	33.28	38.10	71.38	$KMnO_4$ ground to moderately fine powder.
X.	8/25	18	0.7	0.4	34.37	25.16	59.53	$KMnO_4$ ground to moderately fine powder.
XI.	8/28	18	1	0.39	25.20	42.79	67.99	$KMnO_4$ ground to moderately fine powder.

quantity of formalin is too small to produce as vigorous an action as in the other cases.

In Experiment X the proportion of permanganate was increased, with the result that the amount of formaldehyde sent out into the bottle was not affected much, but considerably less remained with the residue.

In Experiment XI the permanganate was decreased to the ratio used by Evans (Maine Board of Health) in the report on his method. The result shows a considerable decrease in the formaldehyde sent out into the bottle and large increase in the amount remaining in the residue.

EXPERIMENTS WITH DILUTED FORMALIN AND PERMANGANATE.

Two experiments were made with 0.6 cc. formalin diluted with 0.3 cc. water and 0.375 gram of powdered permanganate, which are the same proportions as used in most of the experiments in Table II. The procedure was the same as described above.

TABLE VII.

	Date.	Formaldehyde found in bottle. Per cent.	Formaldehyde found in residue. Per cent.	Total found. Per cent.
I.	8/23, 1905.....	31.00	34.23	65.23
II.	8/23, 1905.....	32.16	34.04	66.20

The percentage yield was about the same as that given in Table II, but less than that in the previous experiments (Table VI) with undiluted formalin. The formaldehyde remaining with the residue was about the same as in the previous experiments where powdered permanganate was used. The total formaldehyde found was less than in the experiments with undiluted formalin, indicating a greater destruction of formaldehyde.

UNIVERSITY OF MARYLAND,
BALTIMORE.

THE AMOUNT OF SODIUM SULPHITE RECOVERABLE FROM FOOD PRODUCTS AS A BASIS FOR THE ESTIMATION OF THE AMOUNT ORIGINALLY PRESENT.

BY CLIFFORD D. HOLLEY.

Received April 4, 1906.

AT A time when so many misleading statements are being made concerning sodium sulphite and sulphurous acid as food pre-

servatives and the amounts actually used in the preservation of meats and the bleaching of fruits, it is necessary in order to form an impartial judgment, to make a careful investigation of products actually offered for sale and especially those products which are used extensively. This paper embodies the results obtained by the writer in the Food Laboratory of the North Dakota Experiment Station.

Writers who advocate the use of preservatives would have us believe that sodium sulphite is always used in very small quantities. Dr. Calm, in his treatise on "Sulphurous Acid and Sulphites as Food Preservatives," when discussing the statement that sodium sulphite confers upon minced meat an abnormally brilliant red color, says, "this is not true of the very small amounts of sodium sulphite actually employed on meat, *e. g.*, 0.075 per cent." Again, further on in the same article he repeats this statement adding that 76 to 96 per cent. of this is oxidized to sulphate before the meat is eaten, and from the remaining per cent. of sulphurous acid, the amount naturally present in meat (0.0047-0.01 per cent.) must be deducted, the moiety of free sulphurous acid left in meat preserved by sulphites, is rather startling to those who claim that sodium sulphite as a food preservative is deleterious to health.

In order to determine the accuracy of these statements the following experiments were carried out. The sodium sulphite was added to freshly prepared pork sausage and determinations of the amounts recovered, calculated from the sulphurous acid distilled over, were made, after allowing the meat to stand for the various lengths of time.

TABLE I.—AMOUNTS OF SODIUM SULPHITE RECOVERED.

100 grams pork sausage mixed with 0.2 per cent. sodium sulphite.	After 6 hours.	After 24 hours.	After 36 hours.	After 3 days.
I	49.75	32.43	23.06	23.28
II	26.15	30.85	25.10	22.81
III	33.15	31.75	24.16	22.11
IV	....	....	....	22.45
Average	36.35	31.68	24.11	22.66

Out of forty-three samples of pork sausage and Hamburg steak collected at different butcher shops throughout the state by

E. F. Ladd, Food Commissioner, thirty contained sulphites; of this number, eighteen were examined quantitatively and the following amounts of sodium sulphite, calculated from the sulphurous acid, were recovered. All of the samples were at least thirty-six hours old when analyzed and the majority of them were considerably older, as they had developed the odor of standing meat. Assuming from the above data that as much as one-fourth of the sodium sulphite was recovered, which is stating it very conservatively, the minimum per cent. originally present is given in the last column of the following table.

TABLE II.

100 grams of the samples were treated with phosphoric acid in the usual manner. Lab. No.	Amount of sodium sulphite recovered. Grams.	Minimum. per cent. originally present.
2634, Pork Sausage	0.1315	0.53
2635, Sausage Meat	0.356	1.42
2636, Hamburg Steak	0.3515	1.41
2637, Sausage Meat	0.0294	0.37
2638, Hamburg Steak	0.131	0.52
2648, Sausage Meat	0.0494	0.20
2649, Sausage Meat	0.1206	0.48
2651, Sausage Meat	0.361	1.44
2652, Sausage Meat	0.0356	0.14
2681, Sausage Meat	0.0951	0.38
2683, Sausage Meat	0.0931	0.37
2691, Sausage Meat	0.0894	0.36
2707, Sausage Meat	0.137	0.45
2708, Sausage Meat	0.054	0.22
2710, Sausage Meat	0.0758	0.30
2711, Sausage Meat	0.023	0.09
2734, Sausage Meat	0.044	0.18
2737, Sausage Meat	0.0385	0.15
Average	0.1265	0.50

In order to ascertain the amount recoverable when varying amounts of sodium sulphite were used with the same quantity of sausage, the following experiments were carried out. The meat stood four days after being treated with the sulphite. The distillates were collected in two portions.

TABLE III.

100 grams meat used.	Per cent. first distillate 50 cc.	Per cent. second distillate 100 cc.	Total per cent. recovered.
I 0.2 gram sodium sulphite.....	16.94	6.07	23.01
II 0.3 gram sodium sulphite.....	11.81	6.90	18.71
III 0.4 gram sodium sulphite.....	18.98	3.56	22.54
IV 0.5 gram sodium sulphite.....	17.90	4.85	22.75
Average.....	16.41	5.35	21.75

Several portions of pork sausage were mixed with 0.2 per cent. of sodium sulphite and after standing twenty-four and thirty-six hours were fried in the usual manner and then distilled with phosphoric acid and the sodium sulphite calculated from the sulphurous acid, as usual.

TABLE IV.

Weight of meat, 100 grams.	After 24 hours.	After 36 hours.
I.....	27.72	20.81
II.....	27.08	20.70
III.....	28.22	20.28
Average.....	27.67	20.70

Table IV shows that very nearly as much sodium sulphite is recovered from the fried sausage as from that which has been subjected to the process of distillation only. It is very evident from a study of Table II that surprisingly large amounts of unoxidized sulphite are liable to be taken into the system. For example from laboratory numbers 2635, 2636 and 2651, 0.356 gram, 0.3515 gram and 0.361 gram of sodium sulphite were recovered from 100 grams of meat. Eighty grams of sausage would be easily eaten by an ordinary adult at a meal; this would mean about 0.3 gram of unoxidized sulphite taken into the system in the above instances, along with 1.0 gram, approximately, of sodium sulphate.

ESTIMATION OF COMBINED SULPHUROUS ACID IN DRIED AND EVAPORATED FRUITS.

Fourteen samples of dried or evaporated fruits offered for sale in this state were examined quantitatively for the amount of combined sulphurous acid present. The amount recovered, calculated as sodium sulphite, being given in the following table:

TABLE V.

Lab. No.	Amount of fruit used, 100 grams.	Amount recovered.
2604	Ruby Prunes	0.042
2607	Evaporated Apricots	0.165
2608	Evaporated Peaches	0.115
2617	Evaporated Peaches	0.112
2619	Ruby Prunes	0.190
2620	Dried Apricots	0.149
2640	Silver Prunes	0.046
2653	Silver Prunes	0.086
2666	Silver Prunes	0.110
2685	Silver Prunes	0.226
2730	Ruby Prunes	0.141
2731	Ruby Prunes	0.174
2732	Silver Prunes	0.123
2787	Ruby Prunes	0.054
	Average	0.124

The average amount of combined sulphurous acid calculated as sodium sulphite in the above analyses, approximates very closely that found in the preserved meats and is sufficient to condemn these fruits as an article of diet, when we consider that the amount recovered probably represents only a fraction of the amount originally present.

CONCLUSIONS.

(1) The amount of sulphites mixed with meats to preserve them is much larger than is generally supposed.

(2) The amount of sulphites recovered is approximately one-fourth the amount originally present.

(3) The amount of unoxidized sulphites in fried meats (sausage) is much larger than several writers would have us to believe.

(4) With dried fruits which have been bleached with sulphurous acid, free or combined, the amount remaining unoxidized in the fruit is large, averaging 0.124 per cent. in the above samples. In one instance as much as 0.226 per cent. was recovered, calculated as sodium sulphite.

AGRICULTURAL COLLEGE,
NORTH DAKOTA.

THE APPROXIMATE DETERMINATION OF COMMERCIAL GLUCOSE IN FRUIT PRODUCTS.

By William Lyon.

Received June 21, 1906.

The quantitative determination of commercial glucose in fruit products is of much importance in ascertaining their values commercially, as well as to the official chemist.

The method[1] adopted by the Association of Official Agricultural Chemists for the determination of commercial glucose requires, in addition to a polariscope, facilities which in a small laboratory quite frequently will be found lacking.

Since the soluble solids of fruits in most cases consist largely of sucrose and invert sugar, the approximate quantitative determination of commercial glucose in fruit products can be effected by calculating from the soluble solids and the invert polarization of a sample at the laboratory temperature.

The soluble solids are determined by calculating from the specific gravity of a solution of the product under examination, ascertaining from a table[2] the percentage by weight of solids corresponding to the specific gravity of the sample.

The normal weight of the sample (26.048 grams for the Schmidt and Haensch polariscope) is then clarified, inverted, cooled to the laboratory temperature, made up to 100 cc. and polarized in a 200 mm. tube.

Let a = Percentage of total solids.

b = Polarization in sugar degrees, taken algebraically.

x = Percentage of glucose.

y = Percentage of sucrose and invert sugar.

Then after inversion, assuming that 1 per cent. of commercial glucose causes a rotation of $+1.75°$ and 1 per cent. of invert sugar a rotation of $-0.34°$, at a temperature of 20°, we have:

$$X + y = a$$

$$\text{and } 1.75\,x - 0.34\,y = b$$

$$\text{Whence, } x = \frac{0.34\,a + b}{2.09}$$

Thus a fruit juice containing 70 per cent. of total solids and polarizing $+18°$ after inversion contains approximately 20 per

[1] U. S. Dept. Agr., Div. Chem. Bull. 65, p. 48.

[2] Loc. cit. Table VI.

cent. of commercial glucose. Another fruit juice containing the same amount of solids and polarizing —5° after inversion contains approximately 9 per cent. of glucose.

At 22° [the formula becomes $x=\frac{0.33\ a+b}{2.08}$, and there is a decrease of one in the second decimal of both numbers for each rise of 2° in the temperature.

LOS ANGELES, CAL.

AN IMPROVED CONDENSATION APPARATUS.

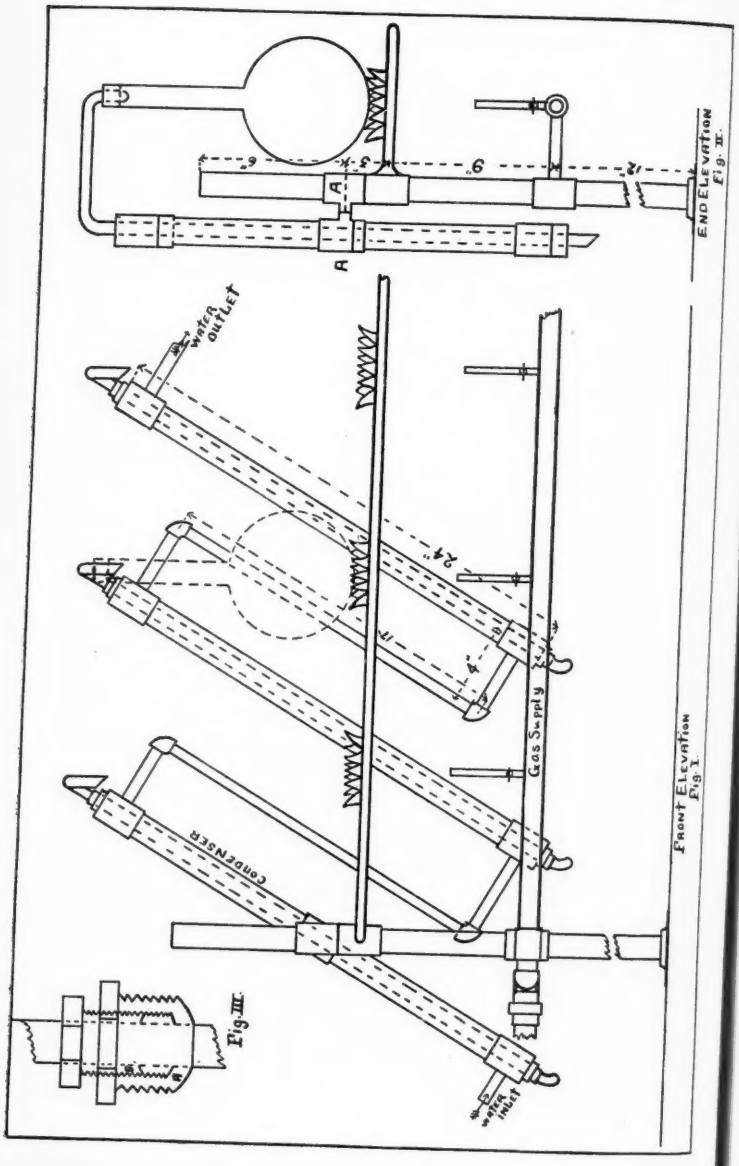
BY H. E. BARNARD AND H. E. BISHOP.

Received June 8, 1906.

FOR some years the earlier form of distillation apparatus, consisting of a copper tank through which the worm of the still passes, has been undergoing modifications and several very satisfactory types have been described which substitute for the condensation tank suitable piping so fitted that the worms pass through the pipe and are thereby constantly subjected to water under pressure.

We have recently designed and constructed a bank of stills, the arrangement of which is different from anything the writers have seen, and which is illustrated by the accompanying working drawings.

The apparatus consists essentially of three parts. The condensers, the support for the flasks and the battery of burners. For the condensers we use inch pipe for the water jackets, and three-eighths pipe for the connection from one jacket to the next. For the top and bottom of the water jacket, ordinary pipe fittings are used, one inch T's with a $\frac{3}{8}$-inch opening. To form a water-tight joint between the water jacket and the block-tin condensing tube, we use an ordinary packing box which is shown at Fig. III in the drawing. It is a brass cup, which fits into the end of the T, which in turn forms the end of the water jacket. B is the jam nut to press the packing against the block-tin tube shown in broken section. The tops of the cup and jam nut are made hexagonal so that they may be turned with a monkey wrench. By studying the drawing at Fig. II, A, it will be noticed that the water jackets are supported by placing a T in the centre of a water jacket tube. This is accomplished by using two short lengths of inch pipe instead of one long length as in the other water jackets.


END ELEVATION
Fig. II.
A
A
9"
9"
9"
2"
water outlet
24"
4"
Gas Supply
CONDENSER
FRONT ELEVATION
Fig. I.
Fig. III.
water inlet

This T is turned at an angle of 90° to the T's at either end of the water jacket; an ordinary $\frac{3}{8}$-inch plug screwed into the T and then a $\frac{3}{4}$-inch by $\frac{3}{8}$-inch cross screwed on to the plug. The threads are reamed out of the cross so that it will slip on the supporting tube easily. The other opening of the cross is filled with a plug with a set screw tapped into it to hold the water jackets in place. The support for the flasks is merely a gas pipe frame covered with galvanized iron. It is attached to $\frac{3}{4}$-inch by $\frac{3}{8}$-inch crosses to hold it in place, as are the water jackets. The openings for the flames are made by slitting the metal in the form of an asterisk (*) and turning up the points in such a manner that they form a springy seat for the round-bottomed flasks. The gas supply pipe is attached to the supporting posts as are the water jackets and the flask support by $\frac{3}{4}$-inch by $\frac{3}{8}$-inch crosses with a plug containing a set screw in one side, and a $\frac{3}{8}$-inch nipple in the other side. The burners are attached to $\frac{1}{8}$-inch air cocks and these are tapped directly into the supply pipe. It will be necessary to rotate this pipe slightly when the burners are raised or lowered. Therefore the support for this pipe is made by reaming out the threads of a $\frac{3}{4}$-inch by $\frac{3}{8}$-inch T and allowing the gas pipe to slip through this T loosely. The connection with the gas supply will hold it in place. The ordinary Bunsen burner will just fit the $\frac{1}{8}$-inch thread on the air cocks, so that no fitting is necessary here.

The posts supporting the apparatus are of $\frac{3}{4}$-inch pipe screwed into ordinary floor plates, which in turn are screwed to the table.

The appearance of the apparatus is greatly improved by a coat of aluminum bronze.

This apparatus possesses several advantages that makes it of value to chemists who have much routine work to do where distillations are required, as in water analysis, nitrogen determinations, alcohol estimations, etc. In the first place, a perfect condensation is always secured, as the water in the condensers is under ordinary hydrant pressure. We employ a gang of 10 stills and even when in constant use, the distillate is always perfectly cold. It takes up but little bench room because of the slanting arrangement of the condensers; the entire apparatus can be readily set up on a bench or shelf not over 12 inches deep, placed against the wall, and the distillates are always in easy reach. All parts are adjustable and any size flasks may be used by raising or lowering their support. The slant of the condenser makes it

possible by rotating the block-tin condensing tube to raise the distillation flask completely from its support. It may then be easily removed without danger of breaking. The apparatus costs but a third as much as when made with copper condensing tank, and is practically indestructible; the materials employed in its construction can be obtained of any plumber or gas fitter and put together with a pipe wrench. Under ordinary conditions the labor and material for a ten-tube still will not cost more than $35.00.

STATE LABORATORY OF HYGIENE,
INDIANAPOLIS, IND.

SOME EXPERIMENTS ON THE DETERMINATION OF VOLATILE COMBUSTIBLE MATTER IN COALS AND LIGNITES.[1]

BY E. E. SOMERMEIER.

Received May 28, 1906.

THE method in general use in this country for the determination of volatile combustible matter is that recommended by the Committee on Coal Analysis appointed by the American Chemical Society.[2] The directions given are as follows:

"Place 1 gram of fresh, undried, powdered coal in a platinum crucible, weighing 20 or 30 grams and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 cm. above the top of the burner. The flame should be fully 20 cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear but the under surface should remain covered with carbon. To find 'Volatile Combustible Matter' subtract the per cent. of moisture from the loss found here."

This is the method used in the volatile determinations made in the Chemical Laboratory of the United States Geological Survey Fuel Testing Plant, the only modification being that the flame is protected from air currents by enclosing in a cylindrical

[1] Published by permission of the Director of the United States Geological Survey. Read before the Columbus Section of the American Chemical Society, May 23, 1906.

[2] This Journal, 21, 1122–1126.

asbestos shield 15 cm. long and 7 cm. in diameter, the platinum triangle being located 3 cm. below the top of the shield. The use of the shield gives more uniformity in the heat treatment with a corresponding greater uniformity of results. It is well recognized that variations in the size of the crucible, tightness of the lid, strength of the flame, etc., affect the process noticeably. Under uniform conditions the same operator usually has no great trouble with duplicates but it is quite probable that different operators working even under only slightly different conditions would have considerable trouble in duplicating results.

In most coals the routine results obtained in the laboratory have checked to within less than 0.3 or 0.4 per cent.; occasionally a sample has given trouble and the variation between duplicates without any apparent reason was as great as 1 per cent. On some lignites it has been found impossible to obtain close duplicates and on a few samples the carrying out of the official method gives very inaccurate results. This may be shown by the results obtained in the laboratory upon two different samples of the same lignite, which samples differed from one another only in the amount of moisture remaining in the air-dried sample and perhaps in the fineness of the grinding. The results on Sample No. 1 are as follows:

Moisture	9.88
Volatile matter	36.17
Fixed carbon	43.65
Ash	10.30
Sulphur	1.30

Sample No. 2.

Moisture	20.24
Volatile matter	58.48
Fixed carbon	10.85
Ash	10.43
Sulphur	1.03

This great difference in the fixed carbon results could not be accidental as all of the results on both samples were duplicated. A series of determinations was begun to determine, if possible, the cause of this great variation. Two causes were suspected and both were found to be partly responsible for the difference. (1) Mechanical loss due to the throwing out of solid particles by the too rapid expulsion of the volatile matter. The pos-

sibility of loss from this source is mentioned in the report of the committee but the results of their experiments are negative. (2) A different breaking down of the hydrocarbon compounds when expelled under different conditions and in the presence of variable amounts of moisture.

The results of Mr. N. M. Austin as published in the committee's report show that a preliminary treatment of the sample at a low heat and then the application of the full flame of the Bunsen burner gives higher results in fixed carbon than where the full flame of the Bunsen burner is applied from the beginning.

The proximate analysis of the sample of lignite giving the unusual results was finally reported by the laboratory as follows:

Moisture	20.24
Volatile matter	35.42
Fixed carbon	33.91
Ash	10.43
Sulphur	1.03

A series of seven results by the official method gave for volatile matter on this sample an average of 62.5 per cent. with a variation between high and low results of over 12 per cent. Three results of volatile matter on this sample made after previous expulsion of the moisture at 105° gave average volatile matter 39.6 per cent. with a variation between high and low results of 5.9 per cent. Preliminary treatment by driving off the moisture and most of the volatile matter at a low heat was then tried, the flame of the Bunsen burner being turned down to 10 cm. and the crucible gradually heated. The application of the heat was regulated by holding the burner in the hand and heating in such a way as to expel the moisture slowly and gradually smoke off most of the volatile matter, the volatile matter escaping freely enough during the last minute of this preliminary heating to burn with a small flame around the edge of the crucible cover. Two results with five minutes of preliminary heating and then seven minutes over the full flame of the Bunsen burner gave an average in volatile matter of 35.08 per cent., the variation between the two results being 0.23 per cent. Two results with three minutes' preliminary heating and seven minutes over the full flame of the Bunsen burner gave an average of 35.6 per cent. with a variation of 0.75 per cent. between results. A result

obtained by four minutes of preliminary heating and then seven minutes over the full flame gave 35.42 per cent. The difference in results obtained by the three, four and five minute preliminary treatment is small and in all subsequent experimental tests the time of the preliminary heating was four minutes. To determine the mechanical losses and difference in volatile compounds given off, a number of ash determinations were made after the driving off of the volatile matter by the official method and after driving off the volatile matter in connection with the preliminary heating. The results of volatile matter and ash on three determinations by the official method are as follows:

Volatile matter	66.72	67.47	54.82
Ash	4.30	4.38	7.25[1]

Two determinations with four minutes of preliminary heating and then seven minutes over the full flame gave:

Volatile matter	36.06	36.65
Ash	11.16	11.15

That mechanical losses occurred during the rapid evolution of the volatile matter by the official method was also indicated by the shower of solid carbon particles driven off as sparks during the first few minutes, while with the preliminary heating these sparks were nearly or entirely absent. The average volatile matter on the first two determinations was 67.1 per cent., the average ash 4.34 per cent. The average volatile matter on the two results by the modified method was 36.35 per cent., ash 11.15 per cent. The moisture in the sample determined at this time was 19.78, giving fixed carbon 32.72 per cent. The difference in the ash results on the two pairs is 6.81 per cent., or the amount of sample driven off mechanically by the regular method is $6.81 \div 11.15$, or 61 per cent. Taking this portion of the fixed carbon result by the modified method gives 20 per cent. as the amount of fixed carbon expelled mechanically in the first determinations. The results on the official process after making this correction and also taking the correct ash value are as follows:

[1] This result is possibly explained by the fact that this sample stood for two hours in the crucible after weighing out and a considerable amount of the moisture content may have escaped before the sample was treated for the determination of the volatile matter.

Moisture	19.78
Volatile matter	47.10
Fixed carbon	21.97
Ash	11.15
	100.00

After making this correction for mechanical losses the difference in the fixed carbon by the two processes is still 10.75 per cent., which difference must be due to the difference in the breaking down of the hydrocarbon compounds by the different heat treatment. The ash from the third result by the official method was 7.25 per cent. or the loss of ash 3.9 per cent. Correction for fixed carbon mechanically carried off is accordingly 3.9/11.15 or 11.4 per cent. The result, after making the fixed carbon and ash corrections, figures as follows:

Moisture	19.78
Volatile matter	43.42
Fixed carbon	25.65
Ash	11.15
	100.00

The difference in this case in fixed carbon by the two methods due to the different heat treatment is 7.07 per cent.

Effect of Fineness of Sample.—This particular sample was very finely ground. To find out how much this difference in result was due to the fineness of grinding, a duplicate portion of the same sample was ground down till it passed a 40-mesh sieve. The results of duplicates by the official method and the modified method obtained are as follows:

	Official method.	Preliminary heating.
Volatile matter	42.07	35.72
Ash	10.25	11.20

Or loss in ash 0.95 per cent. The proximate analysis of the sample by the modified method is as follows:

Moisture	19.35
Volatile matter	35.72
Fixed carbon	33.73
Ash	11.20
	100.00

The correction for fixed carbon to be applied to the result of the official method is 0.95/11.20 or 8.5 per cent. of the fixed

carbon result of the modified method, which is 2.9 per cent. The results by the official method after correcting for mechanical loss of fixed carbon and ash are as follows:

Moisture	19.35
Volatile matter	39.17
Fixed carbon	30.28
Ash	11.20
	100.00

The difference in fixed carbon between the two methods due to different heat treatment is 3.45 per cent. These results show, at least, for lignites that the fineness of the sample has an important effect upon the result. Upon another sample of lignite similar to the one already tested, except that it contained more moisture (30.45 per cent.), the results obtained are as follows:

Average of results by the modified process:

Moisture	30.45
Volatile matter	30.97
Fixed carbon	27.75
Ash	10.83
	100.00

The results in volatile matter and ash by the official method:

Volatile matter	44.40
Ash	8.12

Hence, the correction to be applied to the fixed carbon and ash for mechanical loss is 2.71/10.83. Applying these corrections, the results by the official method are:

Moisture	30.45
Volatile matter	37.43
Fixed carbon	21.29
Ash	10.83
	100.00

The difference in the fixed carbon results between the two samples due to different heat treatment is 6.46 per cent.

To test the effect of the fineness of grinding upon the determination of the volatile matter in ordinary bituminous coal a sample of Kentucky coal containing 2 per cent. moisture, 5.7 per cent. ash and 0.9 per cent. sulphur was still further reduced in ash content by floating on a calcium chloride solution, sp. gr.

1.32. The lighter portion was then thoroughly air-dried and separated by sifting into the following sizes: 1/4 to 1/10, 1/10 to 1/20, 1/20 to 1/40, 1/40 to 1/80 and 1/80 and finer. The proximate analyses of the samples by the official method are as follows:

	Moisture.	Volatile matter.	Fixed carbon.	Ash.
1/4–1/10.....	1.15	39.05	58.20	1.60
1/10–1/20.....	1.45	38.80	58.55	1.20
1/20–1/40.....	1.70	38.55	58.35	1.40
1/40-1/80.....	1.90	38.05	58.40	1.65
1/80 and finer.....	2.05	35.54	59.66	2.75

By the modified process with four minutes of preliminary heating the result in volatile matter on the 1/20 to 1/40 size was 33.75 per cent. and on the 1/80 and finer 32.85 per cent.

The results in volatile matter on these different sizes are somewhat higher on the coarse samples. However, the different ash contents of the different sizes indicate that the sizing had to a degree separated the coal into somewhat different varieties, as the higher ash content of the finer sample would not in itself be sufficient to account for the lower volatile results. In order to see whether the difference was due to the fineness of grinding or difference in the coals, a portion of the 1/20–1/40 sample was ground down in an agate mortar and the volatile matter determined on this fine portion. The average of several results was 37.6 per cent. as against 38.55 per cent. on the coarse sample.

From this series of results it appears, at least in low moisture bituminous coals, that the finer ground samples give somewhat lower volatile matter than the coarser samples, probably due to the more complete sintering together of the fine samples upon heating, with the consequent effect upon the giving off of the volatile matter.

Effect of Different Heat Treatment.—In order to find out how much effect different heat treatment has on different coals, a series of samples was selected ranging from anthracite to peat, most of the samples used in the tests having been previously more or less completely air-dried so as to permit of better handling in the laboratory. Determinations for volatile matter were made in duplicate by the regular official method and by the four-minute preliminary heating method. The proximate analysis of the samples with the volatile matter determined by the official method is tabulated in the first five columns; the results for volatile matter by the preliminary heating are given in the sixth column; the

differences in volatile matter by the two methods are given in the seventh column. The determinations for moisture were all made in accordance with the official method by weighing out a separate sample. The same is true of the determinations for ash with the exception that upon two or three of the lignite samples and one of the Pennsylvania samples the results for ash are those obtained after the determination of the volatile matter by the modified process. These particular samples and results are all specifically mentioned elsewhere in this paper.

Source of coal.	Moisture.	Official method. Volatile matter.	Fixed carbon.	Ash.	Sulphur.	Volatile matter with four minutes' preliminary heating.	Difference.
Colorado anthracite	2.80	5.05	77.55	14.60	0.60	4.90	0.15
Arkansas	0.83	12.47	72.05	14.65	2.14	12.37	0.10
Pennsylvania	0.90	17.35	74.92	6.83	0.97	16.07	1.28
Pennsylvania	1.05	33.10	53.30	12.55	1.76	30.35	2.75
Kentucky	2.99	37.51	56.68	2.82	0.58	34.78	2.73
Indiana	4.20	37.70	45.65	12.45	4.13	34.67	3.03
Washington	6.65	35.87	44.57	12.91	0.68	34.25	1.62
Indiana	8.40	34.40	48.72	8.48	1.47	32.00	2.40
North Dakota (lignite)	11.65	45.58	32.97	9.80	1.04	40.17	5.41
Illinois	12.40	32.18	42.82	12.60	1.30	30.12	2.06
Texas lignite (fine)	19.78	62.50	6.57	11.15	1.03	35.42[1]	27.08
Texas lignite (40-mesh duplicate	19.35	42.07	27.38	11.20	....	35.72	6.35
Texas lignite (not air-dried)	30.45	44.40	15.42	9.73	....	30.97	13.43
Massachusetts peat	13.25	49.80	16.21	20.74	0.58	47.92	1.88

With the exception of the anthracite and semi-anthracite samples, the results by the preliminary heating as compared with the official method all show a considerably less amount of volatile matter and a correspondingly greater amount of fixed carbon. In the case of the lignites, the greater volatile matter by the official method, as has been shown, is partly due to mechanical losses.

[1] Two determinations upon the fine sample of Texas lignite made by heating for four minutes over a flame 5 cm. high and then seven minutes over the full flame (25 cm.) gave 35.47 per cent. volatile matter. Almost an exact check upon the result obtained by the four-minute preliminary heating with a 10 cm. flame regulated by holding burner in the hand.

In order to see if mechanical losses might account for the differences on the bituminous coals, determinations for the ash after the determination of the volatile matter were made on one of the Pennsylvania samples. The average results for ash on the samples by the two methods are as follows:

	Ash.
Official method	12.56
Preliminary heating	12.53

These results indicate no mechanical loss whatever and in none of the samples except the lignites were visible solid carbon particles driven off in the form of sparks, and the differences must be ascribed to the different breaking down of the hydrocarbon compounds by the difference in heat treatment.

Effect of the Presence of Moisture.—Comparisons of the results of volatile matter on a great number of samples differing from one another in moisture content indicate that the presence of loosely held moisture in the sample causes a higher volatile result. In order to obtain more definite data on this question three samples low in moisture and representing widely different kinds of coal were selected for a series of determinations. The effect of loosely held moisture upon the determinations for volatile matter in each of these samples was determined by adding to the sample after weighing out definite amounts of water, which was thoroughly mixed with the sample by means of a fine platinum wire and the volatile determination then made in the usual manner according to the official method. The first sample selected was a sample of Pennsylvania coal. The proximate analysis of the air-dried sample is as follows:

Moisture	1.05
Volatile matter	33.00
Fixed carbon	53.30
Ash	12.55
Sulphur	1.75

The results for volatile matter in this sample determined in the presence of additional moisture are as follows:

	Volatile matter.
With 0.05 gram additional moisture	33.60
With 0.1 gram additional moisture	33.70
With 0.15 gram additional moisture	33.80
With 0.2 gram additional moisture	34.10
With 0.3 gram additional moisture	33.90

The second sample was an air-dried sample of Illinois coal, the proximate analysis of which by the regular official method is as follows:

Moisture	2.35
Volatile matter	39.35
Fixed carbon	44.65
Ash	13.65

The results of volatile matter with the additional moisture added to the sample are as follows:

	Volatile matter.
With 0.03 gram additional moisture	39.60
With 0.05 gram additional moisture	39.30
With 0.10 gram additional moisture	40.00
With 0.15 gram additional moisture	40.05
With 0.2 gram additional moisture	39.75

The third sample was an air-dried sample of Arkansas lignite, the proximate analysis of which by the official method is as follows:

Moisture	10.85
Volatile matter	38.50
Fixed carbon	31.40
Ash	19.25
Sulphur	0.83

The results for volatile matter with the additional moisture are as follows:

	Volatile matter.
With 0.05 gram additional moisture	40.35
With 0.10 gram additional moisture	41.20
With 0.15 gram additional moisture	40.90
With 0.20 gram additional moisture	44.90

Without exception all of these results show that the presence of loosely held moisture in the sample increases the value obtained for the volatile combustible matter. The average increase for the Pennsylvania sample is about 0.7 per cent. On the Illinois sample the increase for volatile matter is 0.4 per cent. On the Arkansas lignite the increase is 3.3 per cent.

To see what effect this loosely held moisture might have on the volatile determinations where the sample was first subjected to four minutes of preliminary heating over a low flame determinations were made upon these samples with and without additional moisture. The results are as follows:

Pennsylvania sample with no moisture added, volatile matter 30.35. With 0.3 gram added, the volatile matter 31.65.

The Illinois sample with no moisture added, volatile matter 34.85. With 0.15 gram moisture added, volatile matter 36.10.

The lignite sample with no moisture added, volatile matter 36.90. With 0.2 gram moisture added, 37.40.

These results show that even with a gradual preliminary heating the presence of loosely held moisture increases the value of the volatile determinations, the difference in some of the samples being as great as the difference by the official method, from which it appears that the rapid application of heat sufficient to drive off this moisture results in a reaction between the water vapor and the carbon or hydrocarbons in the coal.

Conclusions.—The results of the foregoing experiments and tests show that the value obtained for volatile matter in coal is affected to an important degree by the method of heating the sample, by the fineness of pulverization and by the amount of loosely held moisture present. In bituminous coals these differences do not exceed 3 or 4 per cent. and appear to be entirely due to a different breaking up of the hydrocarbon compounds under the different conditions of heat treatment, fineness of sample and amount of moisture present. In the case of lignites where the difference may be as high as 25 per cent. this difference is largely due to the mechanical loss in the sample during the rapid expulsion of the volatile matter.

Correctness of Results.—Since the determination of the volatile matter is a purely arbitrary one unless mechanical loss can be shown, as in the case of lignites, it appears that any results obtained by following out the regulation method should be considered as correct, any difference in results due to differences in fineness of pulverization or to the amount of moisture present having no effect upon the correctness of the value actually obtained. The differences due to difference in pulverization or moisture content do, however, have a very important effect when it comes to the question of different chemists obtaining concordant results upon different samples of the same coal.

In regard to the difference in results obtained due to a different heat treatment, while the method of heating as given by the official method may be considered as giving the correct result it does not necessarily give us a result approximating very closely

the volatile matter as given off when the coal is fired under a steam boiler or especially when coked in a coke oven, as under these conditions the volatile matter is driven off gradually and during a considerable interval of time, and it appears that the slower driving off of the volatile matter from the sample in the laboratory gives results more in accordance with these conditions than does the official method. This latter fact is, however, a matter of minor importance, for so long as all volatile determinations are done in the same way it makes very little difference what that way is.

In the case of lignites where the application of the official method causes mechanical losses it appears desirable and necessary that the committee so modify the official method for volatile matter in lignites as to prevent this loss, and the results of these foregoing determinations and experiments are published at this time with a view of bringing this matter before the committee and the public.

U. S. GEOLOGICAL SURVEY,
FUEL TESTING LABORATORY.

THE RELATION OF SODIUM TO POTASSIUM IN SOIL AND SOLUTION CULTURES.[1]

BY J. F. BREAZEALE.

Received May 12, 1906.

THE determination of the exact amount of salt absorbed from solution by plants during the process of growth has been the subject of many experiments in former years. The ordinary gravimetric or volumetric methods which have usually been employed in such investigations have been on the whole inadequate for such work. The soil solution or the nutrient solution best suited to the requirements of most plants is usually of such a low total salt content that slight changes in its concentration cannot be detected by ordinary analytical means without the expenditure of an amount of time which is almost prohibitive. In the same way the amount of salt a seedling will absorb from solution in the course of a short period of its growth is usually too small to be detected by such methods.

For several years past the Bureau of Soils has been devising and adapting analytical methods which are well suited to such

[1] Published by permission of the Secretary of Agriculture.

investigations.[1] These methods have opened up a comparatively new field for experimental work with the soil and soil solutions and offer a ready means of attacking some of the hitherto difficult problems of plant nutrition.

During the spring and summer of 1905 while engaged in the study of certain soil problems in coöperation with the Rhode Island Experiment Station an opportunity was offered of carrying on, with water and soil cultures, the experiments which are here reported.

The direct object of these experiments was to bring to bear upon the plot work, on the replacement of potassium by sodium, which is being conducted at the Rhode Island Station, the delicate analytical methods as well as the pot and water culture methods used by the Bureau of Soils.[2]

The nature of the plants which had best responded to the application of sodium salts in the field—beets, radishes, turnips, etc.—made it almost impossible to use them in such work; so wheat was selected, as it offered few difficulties in the way of sprouting and handling. The seeds were sprouted on a piece of mosquito netting stretched over a shallow basin of distilled water and kept moist by contact with its surface. When the plumules had reached a length of about 5 cm. the seedlings were transferred to bottles containing the nutrient solutions. The seeds were removed from the seedlings before beginning the experiment, and all further supply of nutrient materials from this source was thus eliminated. With the exception of the first experiment the bottles containing the nutrient solutions were of dark brown glass and held 600 cc. each. "Chemically pure" salts were used to make up these solutions. They were accurately standardized in strengths of 1/5 normal and then diluted to the desired concentrations. The water used in these experiments was shaken up with carbon black and filtered through a Pasteur-Chamberland filter before using.[3] The work was carried on in

[1] "Colorimetric, Turbidity and Titration Methods used in Soil Investigations," Bull. 31, Bureau of Soils, U. S. Dept. of Agric., 1906.

[2] See Annual Reports and Bulletins 104 and 106 of the Rhode Island Experiment Station.

[3] On the beneficial effects of this treatment upon distilled water see Breazeale, J. F.: "Effect of Certain Solids upon the Growth of Wheat in Water Cultures," Bott. Gazz. 41, 54 (1906).

a greenhouse and the solutions containing the cultures were changed every four days.

After much preliminary work, a series of six nutrient solutions was prepared, having the following salt content in parts per million:

TABLE I.

Parts per million.

1.		2.		3.	
$CaCl_2$	44	NaCl	44	$CaCl_2$	44
$MgSO_4$	24	$MgSO_4$	24	$MgSO_4$	24
Na_2HPO_4	38	Na_2HPO_4	38	$(NH_4)_2HPO_4$	38
KNO_3	80	KNO_3	80	$Ca(NO_3)_2$	80
$FeCl_3$	12	$FeCl_3$	12	$FeCl_3$	12
Total	198		198		198

4.		5.		6.	
$CaCl_2$	44	$CaCl_2$	44	$CaCl_2$	44
$MgSO_4$	24	$MgSO_4$	24	$MgSO_4$	24
$(Na)_2HPO_4$	38	K_2SO_4	38	K_2SO_4	38
$NaNO_3$	80	$NaNO_3$	80	$(Na)_2HPO_4$	80
$FeCl_3$	12	$FeCl_3$	12	$FeCl_3$	12
Total	198		198		198

It has already been shown that the concentration of the nutrient solution has an important effect upon water cultures,[1] so care was taken to have each of these solutions of the same total salt content and of a concentration well suited to the growth of wheat. Solution No. 1 was a full nutrient solution, *i. e.*, a solution containing all of the bases and acids usually classified as plant foods. No. 2 contained all of these nutrients except calcium, this element being replaced by sodium. In No. 3 both sodium and potassium were left out and ammonium and calcium substituted. In No. 4 potassium alone was omitted and sodium substituted. In No. 5 PO_4 was replaced by SO_4, and in No. 6 NO_3 was replaced by SO_4. It will be noticed that in making these substitutions acids or bases were used which are known to have but little effect upon the plant. They were added for the sole purpose of bringing up the total salt content.

Sixteen wheat seedlings were placed in 240 cc. of each of these solutions in the manner described in Bulletin No. 23 of the Bureau of Soils and allowed to grow for fifteen days. The solutions were

[1] Breazeale, J. F.: Science, N. S. **22**, 146 (1905), "Effect of the Concentration of the Nutrient Solutions upon Wheat Cultures."

frequently changed so that an abundance of plant food was always present. At the end of this period the plants were taken from the solutions in which they had been growing and each set placed in 240 cc. of a full nutrient solution having the following concentration of nutrients by analysis:

	Parts per million.
Ca (calcium)	27.2
K (potassium)	42.0
PO_4 (phosphates)	51.7
NO_3 (nitrates)	68.8

The salts used in this nutrient solution were the same as those in No. 1 but the amounts were increased slightly in order to have enough left for an analysis after the plants had grown in the solution for the period during which they were under observation. The bottles containing the cultures were then weighed and allowed to stand for two days. At the end of that time they were again weighed, the difference in weight representing the amount of water lost by transpiration. The solutions were then made up to their original volume with distilled water and analyzed for calcium, potassium, phosphates and nitrates.

Table II represents the transpiration of the plants in grams and the amounts, in parts per million, of the nutrients removed from the above-mentioned solution.

TABLE II.

Solution in which seedlings grew during first period.	Transpiration of seedlings and the parts per million of nutrients removed from the full nutrient solution during the second period.				
	Trans.	NO_3.	Ca.	K.	PO_4.
1. Full nutrient	65	40.4	4.0	9.0	9.4
2. Nutrient with Ca left out	47	42.1	6.4	9.0	4.7
3. Nutrient with both K and Na left out	20	10.7	4.0	15.0	0.7
4. Nutrient with K left out	64[1]	53.8	4.8	36.0	6.6
5. Nutrient with PO_4 left out	26	25.8	4.8	6.0	6.6
6. Nutrient with NO_3 left out	29	60.2	3.2	12.0	0.7

The general development of the plants in this experiment was in the same relative order as their transpirations.[2] As indicated by the transpiration figures, the plants in No. 1 were

[1] Owing to an oversight the seeds were not removed from the seedlings of No. 4 until one day after the experiment was begun. This accounts for the relatively high transpiration.

[2] For evidence in regard to the use of transpiration as a criterion here, see Livingston, B. E.: "Relation of Transpiration to the Growth of Wheat," Bot. Gaz. 40, 178 (1905).

more than three times as large as those in No. 3; the proper basis of comparison therefore should be the relative size of the plants. In the absence of the absolute weight of the plants, the data for such a comparison may be obtained by dividing the total amount of the different nutrient constituents taken out of solution by the amount of water transpired by the plants. The following table represents in parts per million the amount of calcium, potassium, phosphates and nitrates removed from the original solution for every 10 grams of water transpired by the plants. Since 240 cc. of water were used, one part per million in the table is equivalent to 24 mg.

TABLE III.

Solution in which seedlings grew during *first* period.	Parts per million of nutrients removed from the nutrient solution during *second* period for every 10 grams of water transpired by seedlings.			
	NO_3.	Ca.	K.	PO_4.
1. Full nutrient	6.21	0.61	1.38	1.45
2. Nutrient with Ca left out	8.95	1.36	1.92	1.00
3. Nutrient with K and Na left out	5.35	2.00	7.50	0.35
4. Nutrient with K left out	8.40	0.75	5.62	1.03
5. Nutrient with PO_4 left out	9.92	1.85	2.30	2.54
6. Nutrient with NO_3 left out	20.76	1.10	4.14	0.24

Using as a basis of comparison the full nutrient solution No. 1, it will be noticed both from Table II and from Table III that in the case of the plants which had been grown for the first fifteen days of their life in a solution from which had been omitted either nitrates, phosphates or potash, these plants, when placed in a full nutrient solution, took up relatively a much larger amount of that particular nutrient which had been left out of the first solution. This is probably also true in the case of calcium, as is indicated in Table II, but is not apparent when calculated on the basis of equivalent plant development as is shown in Table III. For example, No. 6 in Table III, which had been previously grown without nitrates, the seedlings when placed in a solution containing that nutrient took up more than twice as much nitrates as did any of the others. From these results it is apparent that in the manner just described a demand for either of the three most important constituents of mineral plant food, nitrates, phosphates, or potash can be created within the plant and that this demand can be measured by analytical methods.

As indicated in both the preliminary work and in the experi-

ment just described, plants which for the first period grew in a solution containing sodium but no potassium drew less heavily upon the potassium of the full nutrient solution than the plants which for the first period grew in a solution containing neither sodium nor potassium. There was a greater absorption of potassium where sodium had been absent than where it had been present. This seemed to indicate that sodium was in some way affecting the absorption of potassium, and to investigate this question the following experiments were carried out.

Four nutrient solutions were prepared having the following salt content in parts per million:

TABLE IV.

1.		2.		3.		4.	
$CaCl_2$	44	$CaCl_2$	44	$CaCl_2$	44	$CaCl_2$	44
$MgSO_4$	24	$MgSO_4$	24	$MgSO_4$	24	$MgSO_4$	24
Na_2HPO_4	38	$(NH_4)_2HPO_4$	38	$(NH_4)_2HPO_4$	38	$(NH_4)_2HPO_4$	38
KNO_3	80	KNO_3	80	$NaNO_3$	80	$Ca(NO_3)_2$	80
$FeCl_3$	12	$FeCl_3$	12	$FeCl_3$	12	$FeCl_3$	12
Total	198		198		198		198

No. 1 was a full nutrient solution, No. 2 a solution with sodium omitted, No. 3 with potassium omitted, and No. 4 with both sodium and potassium omitted. Eight wheat seedlings were placed in 600 cc. of each of these solutions and allowed to grow for nineteen days with frequent changes of solution. The plants showed marked differences from the first as is shown by the following transpirations.

TABLE V.

No.	Solution.	Transpiration. Grams.
1.	Full nutrient	130
2.	Nutrient without sodium	112
3.	Nutrient without potassium	89
4.	Nutrient without both sodium and potassium	86

After nineteen days the cultures were taken from these solutions and each placed in 600 cc. of a full nutrient solution containing 18.3 parts per million of potassium and allowed to grow for one day. The losses by transpiration were determined, the solutions made up to their original volumes and analyzed for potassium.

Table VI represents the transpiration of the plants, parts per million of potassium removed from solution, and parts per million and milligrams of potassium removed from solution for every 10 grams of water transpired.

TABLE VI.

Results for the second period.

Solution in which seedlings grew during first period.	Transpiration. Grams.	Potassium removed from the nutrient solution.		
			On the basis of 10 grams of water transpired.	
		P.p.m.	P.p.m.	Mgs.
1. Full nutrient solution.....	39.5	8.16	2.06	1.24
2. Nutrient without sodium.....	36.	15.71	4.36	2.61
3. Nutrient without potassium...	26.	12.65	4.86	2.92
4. Nutrient without both sodium and potassium.....	21.1	16.12	7.63	4.58

The plants were then mounted and photographed and are shown in Fig. 1.

It will be seen from the figure and by a comparison of the transpiration results of Nos. 1 and 2 that the presence of sodium has increased the transpiration and size of the plants, and this even where there was an abundance of potassium and all the other necessary mineral plant food constituents in solution. Apparently, a direct need for sodium was manifested by the plants in this experiment. This difference in transpiration and size appeared throughout all subsequent work but is seldom noticed when the seeds are not removed from the seedlings before beginning the experiment. It thus seems that the amount of sodium required by the plants during this period of their growth is small.

The difference in transpiration of Nos. 3 and 4 is much larger than appeared in subsequent work, and indeed somewhat larger than the general appearance of the plants would indicate. As a general rule the effect of sodium in increasing the size of the plant is not marked where there is no potassium present as is clearly shown in the experiments to follow.

It will also be noticed from the table that the phenomenon indicated in the first experiment is brought out more strikingly here. There was a greater demand for potassium in the plants growing in solution No. 2 where sodium was left out during the first period than in those of solution No. 1, which had always had an abundant supply of sodium.

In the following experiment the same number of seedlings were grown for fifteen days in solutions prepared in exactly the same way as those of the preceding experiment. At the end of that time the plants were removed from these solutions and all placed

in a full nutrient solution containing 36.4 parts per million of potassium and allowed to grow for two days. The loss by transpiration was then determined, the solutions made up to their original volumes and analyzed for potassium. Table VII represents the transpiration for two days, the parts per million of potassium removed from solution, and the parts per million and milligrams of potassium removed from solution for every 10 grams of water transpired.

TABLE VII.

	Results for the second period.		
		Potassium removed from the nutrient solution.	
		On the basis of 10 grams of water transpired.	
Solution in which seedlings grew during first period.	Transpiration. Grams.	P.p.m.	P.p.m.	Mgs.
1. Full nutrient solution.....	15.8	1.04	0.65	0.39
2. Nutrient without sodium.....	11.0	6.24	5.67	3.40
3. Nutrient without potassium.....	6.1	5.20	8.52	5.11
4. Nutrient without sodium and potassium	7.8	6.24	8.00	4.80

Here also the comparison of the transpiration figures for Nos. 1 and 2 shows the beneficial effects of sodium upon the plants in the presence of an abundance of potassium. In the case of Nos. 3 and 4, however, this effect is not shown.

As in the previous experiment, the measured demand for potassium is much greater in No. 2 than in No. 1, but not so great as in No. 3, as shown in the third column of the table. This indicates that in water cultures the wheat plant does not absorb as much potassium, even when an abundance of that element alone is present, as it does when an adequate supply of sodium is also present.

Whether the ammonium salt which was substituted in Nos. 2, 3 and 4 played any part in the absorption of potassium was a point that was next considered. Four nutrient solutions were prepared in the manner indicated in Table VIII.

TABLE VIII.

	Parts per million.						
	$CaCl_2$.	$MgSO_4$.	$(NH_4)_2HPO_4$.	$FeCl_3$.	KNO_3.	$NaNO_3$.	NH_4NO_3.
1	44	24	38	12	40	40	0
2	44	24	38	12	80	0	0
3	44	24	38	12	0	80	0
4	44	24	38	12	0	0	80

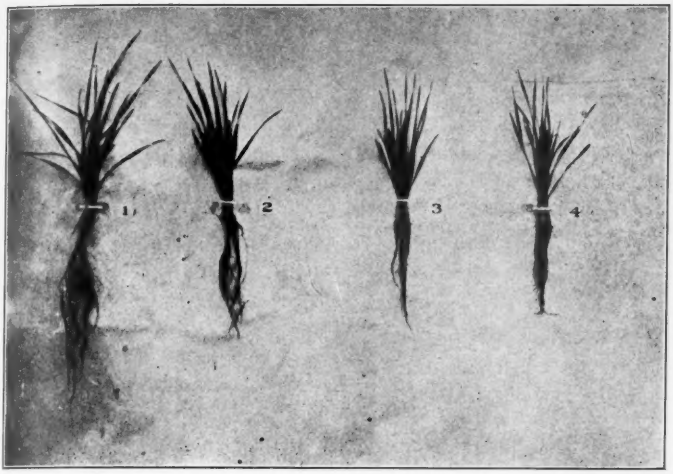


Fig. 1.
No. 1—Full nutrient solution. No. 2—Nutrient without sodium. No. 3—Nutrient without potassium. No. 4—Nutrient without both sodium and potassium.

Fig. 2.
Treatment. Plot No. 16—200 lbs. per acre of sodium chloride; no potassium chloride. Plot No. 22—No sodium chloride; 362 lbs. per acre of potassium chloride. Plot No. 17—200 lbs. per acre of sodium chloride; 362 lbs. per acre of potassium chloride.

Twelve seedlings were placed in 600 cc. of each of these solutions and allowed to grow for seven days. The transpirations for the last day were as follows:

No.	Transpiration. Grams.
1	8.0
2	6.5
3	4.0
4	3.5

The plants were then removed from these solutions and placed in a full nutrient solution containing 73.9 parts per million of potassium, and allowed to grow for four days. The transpirations were then taken, the solutions made up to their original volumes and the amounts of potassium remaining in solution determined. In Table IX will be seen the transpiration of the plants in grams, the parts per million of potassium removed from solution, and the parts per million and milligrams of potassium removed from solution for every 10 grams of water transpired.

TABLE IX.

	Results for the second period.			
		Potassium removed from the nutrient solution.		
			On the basis of 10 grams of water transpired.	
Solution in which seedlings grew during first period.	Transpiration. Grams.	P.p.m.	P.p.m.	Mgs.
1. Full nutrient solution	53.6	12.3	2.3	1.38
2. Nutrient without sodium	46.7	18.5	4.0	2.40
3. Nutrient without potassium	33.5	16.2	4.8	2.88
4. Nutrient without sodium and potassium	34.7	23.0	6.6	3.96

These results are in harmony with those obtained in the earlier experiments.

The results obtained by keeping the plants in solutions in the first period were of such interest that it seemed desirable to ascertain what results would follow if the plants were kept during the first period in the soil itself. To this end about 500 grams of soil were taken from each of three plots of the Rhode Island Experiment Station. These plots are in what is known as the "soda-potash experiment," and have been under observation for the past ten years.[1] Their numbers are given below. They have all received equal yearly applications of nitrogen and phosphates in some combination, with varying amounts of either

[1] See Annual Reports of the Rhode Island Experiment Station.

potassium chloride or of sodium chloride, or both of these salts, excepting in the years 1902–1904, inclusive. The samples taken were given applications of ammonium nitrate and ammonium phosphate at the rate of 350 and 150 pounds per acre respectively, this being about the rate of application for nitrates and phosphates used in the field on these plots in 1905. Potassium chloride and sodium chloride were then added in the amounts indicated in Table X. This soil had been limed twice and was in good physical condition. The soil was then placed in small paraffined wire pots of the form described in Bulletin 23 of the Bureau of Soils, and eight radish seeds planted in each. The soil was kept at the optimum moisture content and the plants allowed to grow for thirty-two days.

The difference in size of the plants can be seen from Fig. 2, the numbers in the photograph corresponding to the plot numbers.

The plants were then carefully taken from the soil, their roots washed clean, and transferred to bottles of a full nutrient solution containing 61.6 parts per million of potassium and allowed to grow for three days longer. They were then taken from the solution and weighed. The solutions were made up to their original volume and analyzed for potassium. Table X represents the plot numbers, applications of potassium chloride and sodium chloride to the soil, green weight of crop, and parts per million of potassium subsequently removed from the nutrient solution for every gram of crop.

TABLE X.

Plot No.	Amount of potassium chloride and sodium chloride added to soil.	Green weight. Grams.	P. p. m. of potassium removed for every gram of green weight.
16.	No potassium chloride, 200 lbs. per acre of sodium chloride...	4.4	5.9
22.	362 lbs. per acre of potassium chloride. No sodium chloride	6.0	4.1
17.	362 lbs. per acre of potassium chloride, and 200 lbs. per acre of sodium chloride.....	11.65	2.5

Plot 16 had not received any potassium for a period of ten years, and this is distinctly shown by the relatively low weight of the crop. The increase in weight of No. 17 over No. 22 is the result of the application of sodium.

Here again as in the solution cultures there was a greater demand for potassium in the plants which had been growing in a soil which had received no potassium than in the plants which had always had a sufficient quantity of that element. There was also a greater absorption of potassium in No. 22 than in No. 17, although in the soil each had the same supply of that element. This indicates, as in the solution cultures, that sodium plays some part in the absorption of potassium. This experiment was repeated as Experiment VI.

The following experiment was similar to the preceding one excepting that soil from plots 4, 10 and 5 was used in this case. These plots corresponded in treatment to plots 16, 22 and 17, respectively, with the exception that plots 4, 10 and 5 had been limed only once. Sixteen radish plants were grown in pots of these soils for twenty-four days. The difference in growth is fairly represented by the following transpirations for one day at the end of that period.

Plot No.	Transpiration in grams.
4	72.
10	105.5
5	120.0

Four plants were selected from each of these plots, placed in a full nutrient solution containing 56.4 parts per million of potassium and allowed to grow for six days. Table XI represents the treatment of the soil, green weight of the plants used, and the parts per million of potassium removed from solution for every gram of green weight.

TABLE XI.

Plot. No.	Amounts of potassium chloride or sodium chloride added.	Green weight. Grams.	P. p. m. of potassium removed for every gram of green weight.
4.	No potassium chloride. 200 lbs. per acre of sodium chloride.....	3.50	7.54
10.	362 lbs. per acre of potassium chloride. No sodium chloride...	2.35	5.10
5.	362 lbs. per acre of potassium chloride, and 200 lbs. per acre of sodium chloride.....	4.44	2.97

As the total weight of the crop is not of interest in this connection, plants were selected which were best suited for solution culture. This accounts for the high weight of the four plants selected in No. 4, the average plant in No. 4 being smaller than in

either of the other two. Here again the need of potassium in the plants of No. 4 is strikingly shown by the relatively large amount of that element which they removed from the nutrient solution. The effect of sodium upon the absorption of potassium is also brought out here.

The experiments just described were performed in the spring and summer of 1905. The plots in the "soda-potash" experiment of the Rhode Island Experiment Station were then in turnips and radishes. These were harvested about the middle of August and the plots planted in beets as a second crop. The plots received at the beginning of the season the full application of fertilizers for the year, *viz.*, 1,000 pounds of dried bone, 20 pounds of magnesium sulphate, and 1,500 pounds of dissolved bone. The quantities of potassium and sodium salts when applied to the plots under consideration here were 362 pounds of potassium chloride, and 200 pounds of sodium chloride per acre. No fertilizers were applied when the beets were planted. When the beets were about two weeks old, four plants were taken from each of the plots before mentioned, their roots washed clean, and placed in 100 cc. of a full nutrient solution containing 43.1 parts per million of potassium and allowed to grow for three days. They were then withdrawn and weighed, the solutions made up to their original volumes and analyzed for potassium.

Table XII represents the applications of potassium chloride and sodium chloride, green weight of plants, and parts per million of potassium removed from solution for every 1 gram of green weight.

TABLE XII.

Plot No.	Applications of potassium chloride and sodium chloride.	Green weight. Grams.	P. p. m. of potassium removed from solution for every gram of green weight.
4.	0 pounds per acre KCl		
	200 " " " NaCl	4.20	1.83
10.	362 " " " KCl		
	0 " " " NaCl	8.55	1.08
5.	362 " " " KCl		
	200 " " " NaCl	9.05	0.85
16.	0 " " " KCl		
	200 " " " NaCl	5.50	4.48
22.	362 " " " KCl		
	0 " " " NaCl	8.00	1.15
17.	362 " " " KCl		
	200 " " " NaCl	9.46	0.0

In this experiment it was apparent, as in preceding ones, that the absorption of potassium from the solution of the second period was strikingly decreased when sodium was present in the solution of the first period.

The procedure employed in this paper, using the plant itself as an indicator, and transferring it from soil to solution or from one solution to another, together with the delicate analytical methods which made it possible to measure slight changes in the concentration of the solution, would seem to be applicable to the study of certain phases of the most important agricultural problems.

BUREAU OF SOILS,
U. S. DEPARTMENT OE AGRICULTURE,
WASHINGTON, D. C.

REACTIONS OF ACETYLENE WITH ACIDIFIED SOLUTIONS OF MERCURY AND SILVER SALTS.

BY J. A. NIEUWLAND AND J. A. MAGUIRE.

Received May 9, 1906.

FROM work already published on the behavior of acetylene towards neutral and acid solutions of mercury and other metals, it is fair to conclude that there is a possibility of forming compounds other than those already mentioned. Up to the present time the only acetylene derivatives of mercury that have been investigated are the nitrates (mercurous and mercuric), the chloride, bromide and the fluoride. It was expected that with acid solutions such as mercury fluosilicate, fluoborate, cyanide, nitrite, chlorate and perchlorate, compounds analogous to those discussed in the previous work,[1] would be formed under proper conditions.

While the work to be described was in progress there came to our notice an article of Hoffman[2] in which, among other compounds, he described the formation of acetylene derivatives of mercuric nitrite, chlorate and perchlorate. His method of preparing these substances is almost identical with the method by which we made them. Besides the substances mentioned by Hoffman, we have been working on a number of others about to be described. The general method of procedure was to make

[1] Thesis: "Some Reactions of Acetylene," Notre Dame University Press, 1904.

[2] Ber. 38, 1899.

the solution of a salt of mercury by treating the acid in question with mercuric oxide and filtering. Care was taken to have these solutions acidified with the acid contained in the radical of the salt. The product was treated with purified acetylene gas that had passed through three Wolff flasks containing in the order mentioned: first, a solution of caustic potash; second, chromic acid; third, some sulphuric acid. The gas was also passed through a drying tower containing small pieces of calcium carbide. The following results were obtained:

Acetylene and Mercuric Chromate.—In a solution of mercuric chromate acidified with chromic acid, acetylene gave instantaneously a bright yellow precipitate resembling lead chromate. The acid solution of the salt was obtained in the following way. To a cold concentrated solution of chromic acid, oxide of mercury was added until no more was dissolved on shaking. After filtering the solution through asbestos, acetylene was passed into it until a precipitate was no longer formed with the gas. The compound was carefully washed for a long time both by decantation and filtration to remove the last traces of chromic acid, and the precipitate dried over sulphuric acid. But in spite of all possible care used in the process of drying, the substance turned brown, aldehyde being one of the products of decomposition. With moist iodine the compound yielded iodoform, especially in an alkaline solution, and when rubbed in a mortar or touched with a warm glass rod, deflagration took place without explosion, and carbon together with the oxide of chromium was deposited. Ordinary acids did not perfectly dissolve the chromate derivative of acetylene, but it readily went into solution in a mixture that yielded nascent chlorine. The following results were obtained in the analysis for mercury:

0.4546 gram of substance gave 0.3736 gram of mercuric sulphide.

0.4062 gram of substance gave 0.3392 gram of mercuric sulphide.

	Calculated for $(OH)C(HC)Hg_2CrO_4$.	Found.	
		I.	II.
Hg	70.42	70.85	71.12

Acetylene and Mercuric Fluosilicate and Fluoborate.—Mercury silicofluoride was prepared by dissolving mercuric oxide in fluo-

silicic acid to saturation. After filtering and passing in acetylene, a white precipitate was formed which towards the end of the reaction began to turn blue, while the odor of aldehyde was very strong. The same results were obtained when acetylene was passed into the fluoborate. These compounds are very unstable, decomposing spontaneously even when dry, into aldehyde and hydrofluoric acid. They respond to the iodoform reaction more readily than any of the other derivatives of acetylene formed in a similar manner. They reacted energetically with dry bromine and chlorine, apparently forming bromine and chlorine substitution products of ethane. Strong hydrochloric acid attacked them, with the formation of the hydrochloride referred to by Keiser[1] and prepared by Polleck and Thummel[2] in another way. It was expected that the following compounds, $\begin{matrix}(OH)CHg\\ |\\ H.CHg\end{matrix}\!\!>\!SiF_6$ and $\begin{matrix}(OH).C.(HgBF_4)\\ |\\ H.C.(HgBF_4)\end{matrix}$, would be obtained, but a qualitative analysis shows, however, that the boron and the silicon of the acids either took no part in the reaction, or were removed by the acetylene, so that the same substance is formed as in the reaction of acetylene with mercuric fluoride. Quite a number of analyses were made but no satisfactory coincident results could be obtained.

Acetylene and Mercuric Chlorate and Perchlorate.—Chemically pure chloric acid was prepared from pure barium chlorate by precipitation with sulphuric acid. Mercuric oxide was dissolved in the acid and acetylene passed into the solution. The white precipitate formed was washed and dried in small quantities over sulphuric acid in a desiccator. Great care had to be used in handling this compound as it was extremely explosive both on contact with sulphuric acid and by percussion or friction. When heated even the smallest quantities detonated with great violence. It gave acetaldehyde on standing in contact with water, and gave the iodoform reaction both with and without alkalies. It decomposed paper and other organic substances, and dissolved in all the acids. It does not explode in the wet state, but slowly decomposes.

Perchlorate of mercury was made from pure perchloric acid and

[1] Am. Ch. J. 15, 535.

[2] Ber. 22, 2863 (1889).

mercuric oxide. The perchlorate of mercury and acetylene resembles the chlorate in every respect, except that it did not explode with sulphuric acid when the compound was washed for a long time, nor even when heated or rubbed in a mortar. The least trace of chloric acid or of mercuric perchlorate in the free state caused violent explosions when thus treated. Analysis of these compounds gave similar erratic results as in the case of the fluosilicate and fluoborate.

Acetylene and Mercuric Cyanide.—When pure acetylene was passed into a solution of mercuric cyanide, made acid with hydrocyanic acid, no precipitate was obtained. If, however, the impure gas that had not been passed through water or sulphuric acid was used, a cream colored precipitate was formed after a few days. As ammonia was given off from the decomposition of the calcium carbide, the solution was slowly made alkaline, causing a precipitate of mercuric carbide. Not enough of the substance was obtained for analysis or thorough examination. The compound was explosive and hence was supposed to be a carbide.

Acetylene and Mercuric Nitrite.—Acetylene gave a heavy cream colored precipitate with mercuric nitrite. If the solution of the nitrite is fairly strong, the reaction after a while becomes so energetic as to give off sufficient heat to effect the decomposition of the compound with the evolution of nitrous fumes and at the same time aldehyde is given off in considerable quantities. In a concentrated solution of nitrous acid and mercuric nitrite, the organic compound is very soluble but can be precipitated by dilution with water. Like the other compounds the nitrite gave an abundant precipitate of iodoform with iodine and an alkali. Analysis of the compound gave the following results:

0.8000 gram of the substance gave 0.7129 gram of mercuric sulphide.

0.4598 gram of the substance gave 0.4100 gram of mercuric sulphide.

	Calculated for $\begin{matrix}C-(HgNO_2)\\ \vert\\ C-(HgNO_2)\end{matrix}$	Found.	
		I.	II.
Mercury.....	77.51 per cent.	76.80	74.49

Acetylene and Mercuric Acetamide.—Acetylene gave a white gelatinous precipitate with mercuric acetamide. Mercuric acetamide was made by dissolving mercuric oxide in an aqueous solution of acetamide, also by melting acetamide, adding the

oxide, and then diluting with water. The substance was found to be of the consistency of jelly, if little or no water was added to the acetamide.

Acetylene and Mercuric Bromate.—Mercuric bromate was made from pure bromic acid and mercuric oxide. It gave a very explosive white precipitate with acetylene, which was not analyzed, whereas the iodate of mercury could not be obtained in the same way.

The general properties of the above compounds may be summed up as follows: Whereas the carbides formed from acetylene in alkaline solutions are explosive, the substances formed in acid solutions are not necessarily explosive unless there is in the compound an acid grouping or radical that is itself unstable, such as that of chloric or perchloric acid. The chromic acid radical, though a strong oxidizing agent, is not violently decomposed when combined with the acetylene, though it is rather unstable. All of these compounds give off aldehyde when heated with very dilute acids or even with water. Some decomposed thus, even when kept perfectly dry in a desiccator over sulphuric acid or in tightly closed bottles. Caustic alkalies break up these compounds into two others, one soluble, the other insoluble in the reagent. The product insoluble in the alkali when treated with iodine, gave tetraiodoacetylene and diiodoacetylene, and resembled the carbide of acetylene, being somewhat explosive. The other substance, soluble in fixed alkalies, is reprecipitated by acidifying the solution containing it. It is the compound which gave the iodoform reaction. These, and other considerations seem to point to the fact that they are substances like those obtained by Polleck and Thümmel[1] by another reaction from vinyl derivatives. Therefore, we have preferred to consider them as derivatives of vinyl alcohol and not of aldehyde. Moreover, if they were acetaldehyde derivatives, the aldehyde, if it reacted with the salts of mercury, should give these compounds. Acetaldehyde forms soluble, not insoluble compounds in presence of mercury salts.

Acetylene and Acidified Silver Phosphate.—Silver like mercury, gave insoluble products with acidified solutions. The compounds formed from acid silver fluoride, acid fluosilicate and acid fluoborate, and from solutions of silver chloride in sodium hy-

[1] Loc. cit.

posulphite, are yellowish precipitates and are all explosive. Silver chromate, though slightly soluble in potassium bichromate and chromic acid, would not give a precipitate with acetylene. Other silver compounds have been prepared from acidified solutions.

Unlike these substances, acid silver phosphate of acetylene is not explosive, in fact it is very stable and only slowly acted upon by light. The solution of silver phosphate was prepared by precipitating from a solution of silver nitrate with disodium phosphate, and dissolving the precipitate in rather strong phosphoric acid. When acetylene was passed into the solution a cream colored substance was thrown down. The silver was quantitatively precipitated, and after saturating with acetylene, no trace of the metal could be found in the solution, which was found to be unchanged phosphoric acid. Light affected the compound only very slowly, for after standing for several months in strong diffused daylight, the color was changed only to a faint lavender. The compound did not give off aldehyde, nor did it respond to the iodoform reaction. It was soluble in potassium cyanide with evolution of acetylene and gave off the odor of hydrocyanic acid. When heated it did not explode, but puffed up, decomposing slowly, leaving finely divided carbon and silver. This substance appears in this respect, to differ from all the silver acetylene derivatives. Analysis of the compound pointed to the following composition. The silver was determined electrolytically, and there was found 44.77 and 44.77 per cent. Calculated for $3(C_2H_2)$, $2H_3PO_4.Ag_3PO_4.H_2O$, 45.3 per cent.

Other Silver Acetylene Compounds.—Besides the acetylene compound of silver phosphate, other derivatives were prepared. When acetylene gas was passed into an acidified solution of silver fluoride, a lemon-yellow precipitate was formed. The substance is paler in color when formed in dilute solution. It is extremely explosive and is probably a compound of silver carbide with silver fluoride. Silver nitrite yields a compound similar in appearance and physical properties. No results could be obtained when acetylene was passed into acidified silver chromate. No compound of silver cyanide and acetylene could be prepared. Silver cyanide was precipitated, washed carefully and redissolved in potassium cyanide. Acetylene gave no precipitate when passed into the solution to which some hydrocyanic acid had been added. The compounds of acetylene with silver bromate

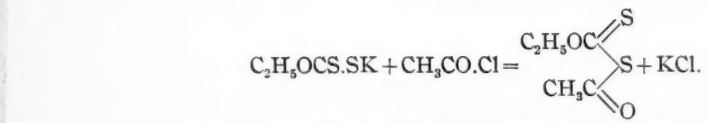
and silver perchlorate were also made. The gas formed precipitates in solutions of these salts acidified with pure bromic and perchloric acids respectively. The perchlorate was prepared by dissolving silver oxide in pure concentrated perchloric acid. Care was taken to have the silver salt strongly acid. When acetylene gas was passed in the solution, a fine crystalline precipitate was obtained. This substance, even in the moist condition, is almost as explosive as nitrogen iodide. On one occasion simple contact of the wet substance with a glass rod resulted in an explosion that shattered the vessel. No smoke or precipitate of carbon accompanies these explosions, thus differing in this respect from the other silver acetylene compounds. These detonations are accompanied with a flash of pale blue light. The smallest quantities of the substance are dangerous. The amount that usually "creeps" up the sides of the vessel in the preparation of the compound, has been known to pulverize the containing beaker when touched with a glass rod. The product formed in very dilute solution is, however, not quite so explosive. Owing to the dangerous nature of this compound, no analysis was attempted. None of the silver compounds of acetylene give the iodoform reaction, and all except the phosphate are quickly blackened by diffuse daylight. Investigation of other metallic derivatives of acetylene is now being made in the laboratory.

CHEMICAL DEPARTMENT, NOTRE DAME UNIVERSITY,
NOTRE DAME, IND.

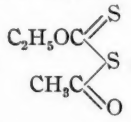
NOTES.

A Preliminary Note on the Reactions between Acid Chlorides and Potassium Ethylxanthate.—In the spring of 1902 the author undertook to study the action of various acid chlorides on potassium ethylxanthate, $C_2H_5OCS.SK$. Owing to press of other work this study has been subject to numerous delays and postponements; it has therefore been deemed advisable to make a preliminary announcement of the work done.

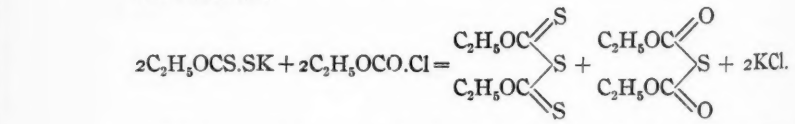
Action of Acetyl Chloride.—The products obtained by the action of acetyl chloride on potassium ethylxanthate vary with slight changes in conditions. Ideally, there should be obtained the mixed anhydride of ethylxanthic and acetic acids according to the reaction



On heating, two molecules of ethylxanthoacetic anhydride should break up to give one molecule of ethylxanthic anhydride and one of thioacetic anhydride according to the well-known rule obtaining with mixed anhydrides of the fatty acids. In practice, however, the reaction takes different courses according to conditions, giving products all of which have not yet been identified with certainty.

When acetyl chloride is added to a well-cooled flask containing potassium ethylxanthate suspended in much ether, there is formed the mixed anhydride  as a very unstable oil which on moderate heating decomposes, not into the simple anhydrides one would expect, but into ethyl acetate, carbon disulphide, and other products. When, however, potassium ethylxanthate is treated with acetyl chloride in the presence of but small amounts of solvent and without cooling, the reaction takes to some extent the normal course; in this way ethylxanthic anhydride was obtained in fairly large amount. The substance was identified by its melting-point (54°), by its properties as described by Welde,[1] and by a sulphur determination which gave 45.91 per cent. S; calculated for $(C_2H_5O)_2C_2S_3$, 45.71 per cent.

Action of Chlorcarbonic Ester.—Chlorcarbonic ester and potassium ethylxanthate react with energy. Besides potassium chloride there is obtained an oil containing ethylxanthic anhydride in solution in smaller amount than one would expect from the reaction:



After complete removal of ethylxanthic anhydride from the

[1] J. pr. Chem. [2] 15, 45.

oily reaction product there is left a complex mixture which has not yet been completely resolved into its constituents.

It is not unlikely that an exhaustive study of these reactions will reveal evidence of the temporary existence of interesting dissociation products, and it is from this standpoint that the reactions will be studied when the work is resumed.

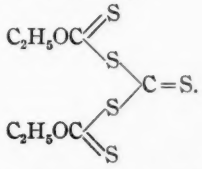
Action of Thiophosgene, $CSCl_2$.—To the calculated amount of thiophosgene contained in a small flask was added an ice-cold water solution of potassium ethylxanthate in proportion to satisfy the equation:

$$2C_2H_5OCS.SK + CSCl_2 = (C_2H_5O)_2C_3S_5 + 2KCl.$$

The water solution became slightly turbid at once, but no further action appeared to take place. The flask was put away in a cool place and occasionally shaken. The lower layer of thiophosgene gradually lost its mobility, becoming finally a dark-brown waxy mass. The water was then poured off and the waxy mass extracted with boiling alcohol. This treatment left undissolved a white crystalline solid soluble in benzene, from which it was recrystallized. Analysis gave the following results: 0.1426 gram substance gave 0.5810 gram $BaSO_4$ (Carius' method). 0.3444 gram substance gave 0.3582 gram CO_2 and 0.1045 gram H_2O.

	Calculated for $(C_2H_5O)_2C_3S_5$. Per cent.	Found. Per cent.
C	29.37	28.36
H	3.49	3.37
S	55.94	55.93

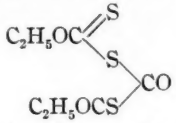
This substance is probably the diethyl ester of the hypothetical pentathiotricarbonic acid, $C_3S_5(OH)_2$:



It crystallizes from hot benzene in microscopic crystals; it melts with decomposition at 160°, and is quite stable toward dilute acids and alkalies. Hot concentrated sulphuric acid decomposes it with liberation of much sulphur. The same substance is immediately precipitated along with potassium chloride

when thiophosgene diluted with acetone is added to an acetone solution of potassium ethylxanthate. The acetone filtrate yields on evaporation a thick, yellowish-brown oil of unknown composition.

Action of Phosgene, $COCl_2$.—From analogy with the result obtained as described above, it was expected that the diethyl ester of the hypothetical tetrathiotricarbonic acid, $C_3S_5O(OH)_2$, would be obtained when phosgene in toluene solution was allowed to act on potassium ethylxanthate; however, none of the compound



was obtained. The reaction is apparently complex. Ethylxanthic anhydride in large amount was found in the reaction product.

OSWIN W. WILLCOX.

SANDY HOOK PROVING GROUND,
FORT HANCOCK, N. J.

Carborundum and Siloxicon.—I have read with considerable interest the account of experiments conducted by Messrs. S. A. Tucker and Alexander Lampen on the measurements of temperature in the formation of carborundum, which appeared in this Journal in its July number.

The methods pursued by them were ingenious, but I would say that the temperature they arrived at was somewhat lower than I had anticipated, although I had not made any definite measurements relating to them.

There seems to be, in the text of their article, some confusion regarding siloxicon. This word I coined as a name of a silicon-oxygen-carbon compound and not for amorphous silicon carbide, as stated by them. The zone of material immediately surrounding carborundum (crystalline carbide of silicon) is mainly or wholly composed of an oxygen compound with carbon as an impurity, this carbon being eventually utilized for the extraction of the residual oxygen and formation of a definite silicon carbide. While this apparent inaccuracy does not in any way detract from the interest and value of their determinations, I can scarcely let such a positive statement of the chemical composition of siloxicon pass unnoticed.

EDWARD GOODRICH ACHESON.

NIAGARA FALLS, N. Y.

REVIEWS.

REPORT OF THE INTERNATIONAL COMMITTEE ON ANALYSIS TO THE SIXTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY AT ROME, 1906.[1]

By A. W. Browne.

Received June 18, 1906.

The International Committee on Analysis appointed by the Fifth International Congress of Applied Chemistry (Berlin, 1903) and subsequently enlarged by the addition of new members selected by the original committee, was composed of 43 members representing 18 different countries. This committee was divided into 11 sub-committees, to which 14 questions were assigned as follows:

(I) (1) Uniform methods for the determination of lead, copper, silver, antimony and zinc.

(II) (2) Uniform materials for use as standards in volumetric analysis, and directions for purifying them and preparing them for weighing.

(3) Uniform manufacture of reagents.

(III) (4) Uniform principles relating to the adjustment and calibration of chemical measuring apparatus.

(8) Uniform principles concerning the adjustment and calibration of instruments for density and percentage determinations.

(9) Adjustment and legalization of balances and weights for chemical purposes.

(IV) (5) Methods of sampling materials for analysis.

(V) (6) Accurate statement of results obtained in fuel investigation.

(VI) (7) Uniform presentation of analytical results.

(VII) (10) Determination of arsenic in wall papers, fabrics, etc.

(VIII) (11) Determination of boric acid, benzoic acid, salicylic acid and other substances employed in the preservation of foods.

(IX) (12) Determination of sulphur in pyrites, blendes, etc.

(X) (13) Is it necessary to calculate the percentage of manganese in a permanganate solution the strength of which with respect to iron is known, by means of a coefficient different from that indicated by the equation?

(XI) (14) Methods of analyzing materials containing tartaric acid.

The statement is made by Dr. G. Lunge, chairman of the committee and editor of the report, that the work upon questions 2, 12 and 13 may be considered complete, or nearly complete;

[1] Edited by Dr. G. Lunge. Pages iv+421. Zurich, 1906. Zürcher & Furrer.

that the work upon questions 1, 4, 5, 6, 7, 8, 9, 10 and 11 has led to the accumulation of much valuable material, but has not yet culminated in the establishment of uniform methods; that one member of the committee only has in each case reported upon questions 5 and 8, and that question 3 has received no attention whatever.

Sub-Committee I. Question 1. Uniform Methods for the Determination of Lead, Copper, Silver, Antimony and Zinc. (Pages 16–70.)—The work in this field has by no means led to the establishment of uniform methods. Considerable progress toward this goal has, however, been made in the study of methods for the determination, respectively, of zinc and of copper. The report embraces (A) a brief general discussion (by G. Chesneau, chairman of the first sub-committee) of the methods usually employed for rapid work in industrial laboratories, or for accurate work in scientific laboratories, together with a brief resumé of the experimental work performed by members of the sub-committee; (B) a discussion, both historical and experimental (by H. Nissenson and W. Kettembeil) of the methods employed in the determination of zinc; (C) an article (by Nissenson) on the importance of uniform, international methods of analysis; (D) a study of the electrolytic method for determination of copper (by A. Menozzi); and (E) a communication (by Nissenson) concerning the methods of assaying employed in the Central Laboratory of the Stock Company at Stolberg. A brief statement of some results obtained in the work upon the determination of zinc and copper should be of general interest.

On the Determination of Zinc.—Two volumetric methods are commonly employed in technical laboratories: titration with sodium sulphide solution, and titration with potassium ferrocyanide solution. The authors propose a slight modification of the latter method as employed by de Koninck and Prost (*Z. angew. Ch.* 1896, 460–468; 564–572). Instead of adding an excess of potassium ferrocyanide at the outset, and then titrating back the cold solution with a standard zinc solution, the authors titrate directly, heating the solutions in order to hasten the reaction. They employ a 1 per cent. solution of uranium nitrate as indicator, but find that a solution of ammonium molybdate containing 9 grams to the liter serves as a satisfactory indicator, reacting more rapidly than the uranium solution, and to certain observers offering a sharper end-point. A comparison of the results obtained by the use of the sodium sulphide method and the ferrocyanide method respectively, shows them to be remarkably concordant. Both methods are also shown to give results agreeing very closely with results obtained both with the gravimetric (precipitation with hydrogen sulphide) method and with Nissenson's (*Z. Elektrochem.* **9**, 761 (1903); *Chem. Ztg.* **27**, 659

(1903)) electrolytic method. Sufficient practical work has not yet been performed to warrant the selection for international use of either method in preference to the other.

The determination of zinc in scientific laboratories is in general accomplished by precipitating the zinc with hydrogen sulphide, preferably from a warm solution acidified with acetic or formic acid. The final treatment of the zinc sulphide obtained is subject to considerable variation in different laboratories. The remarkable agreement obtained by Nissenson between the results from the gravimetric and the electrolytic methods respectively, seems to point toward the latter as the standard method of the future.

For the complete analysis of metallic zinc several different methods have been in use. The method recommended by Nissenson is briefly as follows: 100 grams of the metal are placed in a 750 cc. Erlenmeyer flask provided with a safety tube, and are treated with about 200 cc. of water. Sufficient sulphuric acid is gradually added to maintain a slow evolution of gas. This gas is led into a small Erlenmeyer holding 10 cc. of a solution that contains 7 grams of bromine and 7 grams of sodium hydroxide per liter. When the zinc has almost entirely dissolved, the remaining spongy material is filtered off, and washed until all sulphuric acid has been removed. The amount of iron in the filtrate is determined by titration with permanganate. The spongy material is dissolved in nitric acid. A precipitate at this point may be caused by tin or by large amounts of antimony. If no precipitate appears, the solution is treated with 12 cc. of dilute sulphuric acid, and evaporated until white fumes appear. After the separation and determination of the lead, the filtrate is warmed and treated with hydrogen sulphide. The precipitate is filtered off, allowed to stand in a cold solution of sodium sulphide for some time, and is filtered. In the filtrate antimony is precipitated with sulphuric acid, allowed to subside, filtered off, and dissolved in concentrated hydrochloric acid. The solution is boiled until all hydrogen sulphide is expelled, treated with from 15 to 20 cc. of dilute hydrochloric acid, and is titrated while boiling hot with potassium bromate, indigo being used as indicator (*Berg. hüttenmänn. Ztg.* **62**, 421 (1903)). The residue left after the above-mentioned treatment with sodium sulphide is dissolved in nitric acid. The solution is almost neutralized with ammonium hydroxide, and is treated with ammonium carbonate until it reacts alkaline. After it has been standing (warm) for several hours the bismuth carbonate is filtered off and is dissolved in a few drops of sulphuric acid. The solution is evaporated until white fumes appear in order to remove the last traces of lead. The bismuth is once more precipitated, and is finally determined as Bi_2O_3. If copper is present in the filtrate from the first bismuth precipitate, this solution is decolorized with potassium cyanide.

Cadmium is precipitated with sodium sulphide, is filtered off and is weighed as CdO, while from the filtrate copper sulphide is precipitated by cautious addition of acid. The filtrate from the hydrogen sulphide precipitate is boiled to expel hydrogen sulphide, is oxidized and is treated with ammonium hydroxide. Iron is determined after a second precipitation. The filtrate from the first iron precipitate is acidified, and is treated (hot) with a few drops of barium chloride solution. The barium sulphate is removed by filtration. The barium remaining in the filtrate is precipitated with sulphuric acid, and is filtered off. The hot solution is treated with hydrogen sulphide. The arsenious sulphide is filtered off, and if it still contains antimony is treated with cold ammonium carbonate. The solution is again filtered. The arsenic in the filtrate is precipitated with dilute sulphuric acid, is filtered off, and after being dissolved in hydrochloric acid, to which some potassium chlorate has been added, is precipitated with magnesia mixture. This method is commendable in that a single 100-gram sample suffices for the determination of all ordinary impurities and in that provision is made for the determination of bismuth, an operation that has been neglected by authors of previously published methods. Nissenson believes that the percentage of zinc itself is best determined by difference. Chesneau, however, cautions chemists against the extension of this indirect method to other cases, however applicable it may in the case of zinc. He is of the opinion that the percentage of each impurity and the percentage of the metal itself should in each case be directly determined.

On the Electrolytic Determination of Copper.—This subject is discussed by A. Menozzi who has made an experimental study of the various conditions governing the deposition of copper for analytical purposes. The negative electrodes employed in the work comprised two platinum dishes with a capacity of from 100 to 150 cc., with an inside surface of from 100 to 125 sq. cm., and weighing from 60 to 62 grams; two cones with a working surface of 160 sq. cm., and weighing from 22 to 29 grams; a cylinder with a total surface of 260 sq. cm., weighing a little over 54 grams, and a cylinder of platinum gauze, with a surface of about 145 sq. cm., weighing 12 grams. Platinum spirals, discs and gauzes served as positive electrodes. Especial emphasis is laid upon the desirability of employing the rotating anode. For this work the electrodes of Classen are well adapted, while the gauze electrodes of Winkler are unsatisfactory. The stirring apparatus of Fischer and Boddaert was employed. The author's results may be summarized as follows: (A) Deposition from acid solution. A nitric or sulphuric acid solution should be employed. The amount of copper deposited should not exceed 1 gram in weight. From 2 to 5 volumes of concentrated nitric acid or from 3 to 5 volumes of sulphuric acid are added to 100 volumes of

the electrolyte. The mean tension of the current for ordinary electrolysis should be from 1 to 3 volts; for electrolysis with rotating electrode, from 3 to 4 volts. The amount of current for ordinary electrolysis is from 0.1 to 0.5 ampere; for electrolysis with rotating electrode, from 4 to 5 amperes. The presence of an excess of nitric acid, or of chlorides, organic acids, arsenic, antimony, bismuth, mercury, silver or tin, is detrimental. Agitation of the liquid (by rotating electrode) remarkably facilitates the deposition of the copper. Heating the electrolyte favors the deposition of copper, but if the temperature is raised too high, removal of the last traces of copper becomes almost impossible. The deposit must be rinsed with water, alcohol, and alcohol and ether, without interrupting the current. The deposition requires from three to twelve hours when the ordinary method is employed; with the rotating electrode it requires about one hour. The end-point may be determined by testing the electrolytic solution for copper by the usual chemical methods, or by means of an auxiliary electrode. Copper may be separated by the electrolytic method from alkali and alkaline earth metals, from zinc, cadmium, nickel, cobalt, aluminum, chromium, iron (if present in small quantities) and from lead and manganese (in presence of an excess of nitric acid). One of the principal difficulties connected with the electrolytic precipitation of copper is to obtain, in acid solution, a complete deposition of the last traces of the metal. Some laboratories overcome the difficulty by concentrating the solution toward the end. Menozzi prefers to determine the residual copper colorimetrically, after treating the solution with ammonium hydroxide. (B) Deposition from alkaline solution. A nitrate, sulphate or chloride solution should be employed. The amount of copper deposited should not exceed 1 gram in weight. Sufficient ammonium hydroxide is added to redissolve the precipitate at first formed. Then more ammonium hydroxide (0.96) is added, from 20 to 25 cc. for a solution containing 0.5 gram of copper, and from 30 to 35 cc. for a solution containing 1 gram of copper. From 3 to 4 grams of ammonium nitrate are also added. The mean tension of the current for ordinary electroylsis is from 2 to 4 volts; with rotating electrode it is from 3 to 5 volts. The amount of current for ordinary electrolysis is from 0.1 to 0.5 amperes; with rotating electrode it is from 4 to 5 amperes. The presence of lead, bismuth, mercury, cadmium and nickel is detrimental. Agitation of the liquid (by rotating electrode) accelerates the deposition of copper. Heating is to be avoided. The deposited metal should be washed without interrupting the current. Precipitation requires from four to twelve hours by the ordinary method; with the rotating electrode it requires from one to two hours. The action may be considered complete when the solution has completely lost its color.

Sub-Committee II. Question 2. Uniform Materials for Use as

Standards in Volumetric Analysis, and Directions for Purifying Them and Preparing Them for Weighing. (Pages 71–153.)—The report of work accomplished in this field embraces a general statement by W. Fresenius (chairman of the second sub-committee), and two articles of considerable length already published elsewhere ("Beiträge zur chemisch-technischen Analyse," *Z. angew. Ch.* **17**, 195–203; 225–236; 265–270 (1904). *Centrbl.* 1904, I, 1036. "Zur Frage der Einstellung von Normalsäuren für Massanalyse," *Z. angew. Ch.* **18**, 1520 (1905); *Chem. Centr.* 1905, II, 1284) by G. Lunge. Other articles published ("Zur Frage über einheitliche Titersubstanzen (Urtitersubstanzen)," S. P. L. Sörensen, *Z. anal. Ch.* **44**, 141 (1905); "Uber die Anwendung von Natriumkarbonat und Natriumoxalat in der Acidimetrie," S. P. L. Sörensen und A. C. Anderson, *Z. anal. Ch.* **44**, 156 (1905), **45**, 217 (1906); "Zur Frage der Titerstellung von Normalsäuren," J. Sebelien, *Chem. Ztg.* **29**, 638 (1905)) by members of this sub-committee have been briefly reviewed in the chairman's report. In the opinion of W. Fresenius it may now be regarded as an established fact that either sodium carbonate (when prepared according to Lunge's directions) or sodium oxalate (ignited either over an alcohol flame, or a gas flame so applied that the products of combustion cannot come into contact with the salt) may be employed as standard materials for use in acidimetry, even in work requiring a high degree of accuracy.

Preparation of Sodium Carbonate for Use in Standardizing Acid Solutions.—The material selected should be of a pure white color, and should dissolve in water forming a perfectly clear solution. In quantities of from 1 to 2 grams it should give no reaction for sulphates, and with silver nitrate should give no more than the faintest opalescence. By heating, it is possible to insure the removal of water, and of any excess of carbon dioxide that may be present. If the temperature is too high, Na_2O may be formed. The fortunate circumstance that there is a considerable range of temperature through which the material may be heated without danger, gives to sodium carbonate the preference (according to Lunge) over all other substances hitherto suggested as the basis for standardization of acids. A platinum dish half filled with the material is so placed upon a sand-bath that the sand surrounds it to the height of the sodium carbonate within. The heating should be rapid until the temperature of 270° is reached, when it should be continued more slowly for one-half hour, during which time the temperature should not be permitted to rise above 300°. During this process the substance should be frequently stirred with a platinum spatula or with a flattened glass rod.

Preparation of Sodium Oxalate for Use in Standardizing Acid Solutions.—According to Sörensen's directions, the material is first precipitated with alcohol and dried at 240°. The sodium oxalate employed in the experiments of Lunge was obtained from

Kahlbaum, who had prepared it in this way. In order to obtain the greatest accuracy it is advisable to dry the salt in a water-bath drying-closet for some time before weighing. Lunge dried the salt for two and one-half hours, and then allowed it to cool in a desiccator for two hours. About 0.5 gram of the sodium oxalate is now weighed out into a platinum crucible provided with a cover, and is heated until complete transformation to sodium carbonate takes place. In one-fourth to one-half hour, according to Lunge, the change is complete, but the crucible should then be heated to a higher temperature in order to oxidize the small quantity of carbon liberated during the process. During this last operation the crucible should be left partly uncovered. As source of heat should be employed either an alcohol flame or a gas flame so applied that the products of combustion cannot come into contact with the salt. According to Lunge, the crucible should be set upon an asbestos plate through which a hole of proper size has been cut. If this precaution is not taken, the sulphur compounds in the illuminating gas will react with the sodium carbonate, introducing an appreciable error in the final result. After the ignition has been completed, the sodium carbonate is moistened with water and is then treated with the acid to be standardized.

The use of methyl orange as indicator is recommended in all cases except those in which a weak acid is involved. Phenolphthalein gives a sharper end-point, but necessitates a more complicated procedure. The nitrophenols and ferric salicylate show no superiority over methyl orange.

Pure iodine is still recommended as the basis of iodometric titrations. Potassium biiodate of constant composition may not be readily prepared. For the standardization of potassium permanganate Lunge has found that with certain precautions any one of the four following substances may be employed: (1) oxalic acid, (2) iron wire, (3) sodium oxalate and (4) hydrogen peroxide (by the nitrometer method).

Sub-committee III. Question 4. Uniform Principles Relating to the Adjustment and Calibration of Chemical Measuring Apparatus.—The report upon this subject consists in a series of regulations (stated in German, French and English) classified as follows:

International regulations concerning chemical measuring apparatus.

I. Measuring Vessels for Volumetric Analysis.
   A. General Rules.
   B. Shape and Calibration.
   C. Particular Rules.
   D. Limits of Error.

II. Measuring Apparatus for Gas Analysis.
   A. General Rules.

B. Shape and Calibration.
C. Limits of Error.

Question 8. Uniform Principles Concerning the Adjustment and Calibration of Instruments for Density and Percentage Determinations.—Under this head is given (in German, French and English) a series of regulations classified as follows:

International Regulations Concerning Hydrometers.
A. General Rules.
B. Shape and Calibration.
C. Special Hydrometers.
D. Limits of Error.

Question 9. Adjustment and Legalization of Balances and Weights for Chemical Purposes.—The report upon this subject presented by H. W. Wiley contains an account, both historical and descriptive, of the United States standards of weight and measure, together with a brief statement concerning the purpose of the Bureau of Standards. Reference is made to the method of T. W. Richards (this Journal, **22**, 144 (1900)) for standardizing weights.

Sub-committee IV. Question 5. Methods of Sampling Materials for Analysis. (Pages 190–220.)—The chairman of the fourth sub-committee, Dr. H. W. Wiley, has presented a report containing a detailed discussion of the topics mentioned in the following summary:

Part I. General Principles of Sampling.—(Applied to the sampling of gases, liquids and solids.)

Part II. Sampling Special Classes of Materials.

Soils.—General principles. General directions for sampling. Sampling with an auger. Sampling for moisture determination. Sampling to determine the permeability of soil to water or air. *Treatment of sample.* Air-drying.

Fertilizers.

Minerals Containing Fertilizing Materials.

Mixed Fertilizers. Barn-yard Manures.

Materials used for Road Building.

Food Products.—Dairy products (butter, milk and cheese). Sugars and molasses. Cattle foods. Insecticides. Foods. Drugs and chemicals (including (1) gummy substances, (2) powders, (3) crude vegetable drugs, (4) liquids, (5) goods solid at ordinary temperatures, but liquefied on warming, and (6) articles that congeal in part or as a whole at low temperatures.)

Sub-committee V. Question 6. Accurate Statement of Results Obtained in Fuel Investigation. (Pages 221–225.)—A brief and incomplete discussion of several questions bearing upon the analysis and testing of fuels. Among these questions may be mentioned the following: In what way may the results of a fuel examination be most intelligibly expressed? For example, should the higher or the lower heating value be reported; should

the percentages of hydrogen and oxygen be directly reported, or should they be calculated as available hydrogen and chemically combined water? In what way should the percentage of sulphur found by analysis of the coal be reported? Should the amount of water formed by combustion of the coal be determined directly from combustion in the bomb, or should it be calculated from the ultimate analysis? What directions should be given with respect to the degree of comminution of the coal, the method of sampling, etc.? What directions should be given with respect to technical fuel tests and other methods for the determination of calorific value aside from the bomb-calorimeter method?

Sub-committee VI. Question 7. Uniform Presentation of Analytical Results. (Pages 226–279.)—The report upon this subject contains a discussion of various methods for expressing the results of analysis, to be used in the following lines of work:

I. For purely scientific analysis.
   (1) The establishment of chemical composition.
   (2) Determination of formulae.
   (3) Gas analysis.
   (4) Inorganic salts and the salts of metals with organic acids.
   (5) Double salts and complex compounds.
   (6) Mixtures, pigments, glass, cement, gunpowder, etc.
   (7) Minerals and rocks.
   (8) Organic substances.

II. Analysis of materials used in the trades and industries.
   (1) Products of the chemical industries.
   (2) Metals, ores and minerals.
   (3) Inorganic and organic dye-stuffs.
   (4) Medicines and pharmaceutical products.
   (5) Foods, beverages, perfumes and photographic materials.

III. Analysis of solutions.
   (1) Natural and artificial mineral waters.
   (2) Drinking water.
   (3) Solutions in general.
   (4) Urine analysis.

Sub-committee VII. Question 10. Determination of Arsenic in Wall-paper, Fabrics, Etc. (Pages 280–318.)—The report embraces articles upon the following subjects: (1) Electrolytic Method for the Estimation of Arsenic in Wall-paper, Fabrics and Similar Materials, by Chairman T. E. Thorpe; (2) Experiments on the Determination of Small Amounts of Arsenic Acid by Iodometric Acidimetry, by P. Klason and J. Köhler; (3) Quantitative Method for the Determination of Small Amounts of Arsenic in Commercial Articles, by J. Köhler; (4) Report of Estimation of Arsenic in Wall-papers, Tissues, etc., by H. W. Wiley.

(1) This method involves the use of an apparatus already described by the author (*J. Chem. Soc.* **83**, 974 (1903)). A weighed portion of the sample to be analyzed (usually about 2 grams) is treated in a platinum dish first with a little hot water, then with 20 cc. of arsenic-free lime-water and 0.5 gram of calcined magnesia. The material is next heated until the organic matter is thoroughly charred, when the dish is placed in a muffle furnace and heated until the carbon has been burned off. When cold the ash is moistened with water and is treated with 20 cc. of dilute sulphuric acid. After it has been warmed the material is transferred to a flask of about 120 cc. capacity. Half a gram of potassium meta-bisulphite is added, and the solution is boiled until free from sulphurous acid. The solution is now cooled, and is diluted to 50 cc. An aliquot portion is then taken for use in the apparatus. In order to admit of convenient comparison with standard deposits of arsenic, the deposit from the solution under consideration should contain not less than 0.005 mg. nor more than 0.0125 mg. of arsenic. Further details concerning the manipulation of the apparatus and the preparation of the standard deposits are given in the article.

(2) The work upon this subject embraces experiments upon (*a*) the direct titration of arsenic acid with $n/2$KOH; (*b* and *c*) the titration of arsenic acid by iodometric acidimetry; (*d*) the temperature to which small amounts of arsenic acid may be heated without loss; (*e*) the oxidation of arsenious to arsenic acid; (*f*) the titration of arsenic acid after distillation of the arsenic as trichloride; (*g*) the determination of small amounts of arsenic in paper; (*h*) the determination of arsenic in wool; (*i*) the stability of very dilute ($n/1000$ to $n/500$) hyposulphite solutions; (*j*) the stability of $n/500$ iodine solution. The principal points of interest in the experiments may be briefly stated as follows: (*a*) This method was found to give only approximately correct results, (*b* and *c*). This method is based upon the addition to the acid of a solution containing 1 equivalent of potassium iodate and 5 equivalents of potassium iodide. The amount of iodine liberated is determined by means of a hyposulphite solution. With proper precautions accurate results were obtained by the authors with a series of solutions containing from 0.067 mg. to 203.01 mg. of arsenic. The method is to be recommended provided organic substances are absent. (*d*) It was found that small amounts of arsenic acid (0.676 mg.) could not be heated to a temperature above 100° for a long time (several hours) without loss, probably due to reduction effected by dust particles in the air. (*e*) Nitric acid alone will not completely oxidize arsenious to arsenic acid, but will do so in presence of hydrochloric acid. (*f*) The temperature must be raised rapidly in order to prevent loss of hydrochloric acid before the temperature is reached at which distillation of the arsenic trichloride commences. (*i*) After ten days the loss

undergone by the $n/500$ solution was 3.9 per cent.; after seventeen days the loss in the case of the $n/1000$ solution was 12.7 per cent. (*j*) After thirty-two days the loss was 1.14 per cent.

(3) In this article is described a series of experiments intended to supplement the work of Klason and Köhler, with a view to eliminating the difficulties arising when organic matter is present. The procedure is essentially as follows. The arsenic is either converted into the trichloride by distillation with hydrochloric acid and then into arsenic acid by nitric acid, or it is precipitated as arsenious sulphide and then oxidized by nitric acid. After it has been evaporated to dryness the arsenic acid is treated with potassium permanganate (2 cc. 5 per cent. solution, with 1 cc. 30 per cent. sulphuric acid) in order to eliminate organic matter. It is then heated over a water-bath ten to fifteen minutes, and is reduced with sulphurous acid (10 cc. 7 per cent. solution). The sulphurous acid is removed by heating for thirty minutes to a temperature of 50–70°, and then to 100°. This treatment is repeated with 5 cc. of sulphurous acid, and the solution is again evaporated until complete removal of the sulphurous acid has been effected. If the liquid is not perfectly clear after the first treatment, oxidation with permanganate should be repeated. The residue is dissolved in 15 cc. of water, is neutralized with sodium bicarbonate, and is titrated with $n/500$ iodine solution. Starch is added, and the solution is vigorously shaken during the titration. The bicarbonate solution alone requires about 2 drops of the iodine solution before the blue color appears. The color remains but a few seconds. The method has been tested by seven different chemists with satisfactory results.

(4) This article contains a description of the method employed in the Miscellaneous Laboratory of the Bureau of Chemistry for the determination of arsenic in wall papers and fabrics. A full account of this method, which is essentially a modification of the method of Sanger (*Pr. Am. Acad.* N. S. **18**, 24 (1891)) has already been published. (Bulletin 86, Bureau of Chem. U. S. Dept. Agr. (1904)). Some use has been made of the electrolytic method of Thorpe (described above) in the Bureau of Chemistry. Most excellent results were obtained.

Sub-committee VIII. Question 11. Determination of Boric Acid, Benzoic Acid, Salicylic Acid and Other Substances Used in the Preservation of Foods. (Pages 319–343.)—The report includes two articles (1) by M. L. Lindet, chairman of the sub-committee, and (2) by H. W. Wiley.

(1) A general discussion is given in this article of the methods employed in the determination of the following substances: salicylic acid, benzoic acid, boric acid, borax, fluoborates, fluorides, alkaline fluoborates, alkaline fluosilicates and formaldehyde.

(2) In this paper is given a detailed description of the methods now used in the Bureau of Chemistry for the detection and deter-

mination of the following substances: formaldehyde, sulphurous acid, salicylic acid, saccharin, benzoic acid, boric acid and the borates, fluorides, borofluorides and silicofluorides. An account is also given of the methods used in the detection of coloring-matter in foods, in the determination of annatto in butter or other fat, and in the detection of coloring-matter in milk.

Sub-committee IX. Question 12. Determination of Sulphur in Pyrites, Blendes, Etc. (Pages 344–399.)—This report consists in the main of two articles, both of which have already been published elsewhere: (1) Determination of Combined Sulphuric Acid by the Methods of Lunge and of Silberberger, by G. Lunge (*Z. angew. Ch.* **18**, 449 (1905)). (2) On the Determination of Sulphuric Acid by Precipitation with Barium Chloride in Presence of Interfering Substances, by G. Lunge and R. Stierlin (*Z. angew. Chem.* **18**, 1921 (1905)). By referring to the following additional articles (Silberberger, *Ber.* **36**, 2755 (1903); Lunge, *Ibid.* p. 3387; Silberberger, *Ibid.* p. 4259; Lunge, *Z. angew. Ch.* **17**, 913 and 949 (1904); Küster, *Ibid.* p. 1180; Lunge, *Ibid.* p. 1180; Pattinson, *J. Chem. Ind.* **24**, 7 (1905); Hintz and Weber, *Z. anal. Chem.* **45**, 31 (1906); Dennstedt and Hassler, *Z. angew. Ch.* **18**, 1562 (1905); Lunge, *Ibid.* p. 1656; v. Knorre, *J. Chem. Ind.* **28**, 2 (1905)), more complete information concerning the method of Lunge may be obtained. This method is recommended by the ninth sub-committee for international use in the determination of sulphur in pyrites, blendes, etc.

Sub-committee X. Question 13. Is it Necessary to Calculate the Percentage of Manganese in a Permanganate Solution, the Strength of which with Respect to Iron is Known, by Means of a Coefficient Different from that Indicated by the Equation? (Pages 400–418.)—As a result of the experimental work performed by himself and his coworkers, chairman L. L. de Koninck draws the conclusion that it is possible, under conditions easily established, to obtain a sharp reaction between potassium permanganate and manganese salts, in the ratio $3MnCl_2 : 2KMnO_4$. It is therefore unnecessary to employ an arbitrary coefficient in calculating the strength of a permanganate solution from the analytical results obtained by a suitable modification of the Guyard method. The procedure adopted by de Koninck in proving his contention is essentially as follows: A measured volume of permanganate solution is reduced by heating with hydrochloric acid. The moderately acid manganous solution thus obtained, to which pure ferric chloride has been added, is treated at a slightly elevated temperature with zinc oxide suspended in water, until the point is reached at which further addition of the oxide effects a rather sudden coagulation of the precipitate. The supernatant liquid after it has been shaken (and warmed, if necessary) is completely clear and colorless, or at least only slightly milky. After diluting to about 300 cc. and adding in the majority of cases 20 grams of

zinc sulphate the author titrates the solution at about 100° with the permanganate solution (of which a portion was reduced at the outset) until a pink color is obtained which persists even after the solution is boiled. The volume of permanganate solution required was in every case almost exactly two-thirds that of the permanganate solution reduced. This is obviously in accord with the ratio $3MnCl_2 : 2KMnO_4$. The author recommends for actual work a procedure somewhat as follows: A sample of manganiferous iron ore (for example) is dissolved in hydrochloric acid; the filtered solution, moderately acid, is diluted to 500 cc. Two samples of 100 cc. each are taken from this solution. To one of these samples is added the manganese chloride obtained by reduction of a measured volume of the permanganate solution with hydrochloric acid. After the iron has been removed from both samples by the addition of zinc oxide, the solutions are titrated with permanganate. From the difference the strength of the permanganate solution may be calculated, while from the lower result may be obtained the percentage of manganese in the sample.

The report upon this question contains also an article by G. Chesneau which has been published elsewhere (*Annales des Mines*, Feb. (1906)). This piece of work contains some experimental evidence corroborating the conclusions of de Koninck.

Sub-committee XI. Question 14. Methods of Analyzing Materials Containing Tartaric Acid. (Pages 419–421.)—For the determination of bitartrates it is proposed to abandon the method of direct titration without filtration. The approved method is briefly as follows: In a 500 cc. flask is placed 2.35 grams of the fine material, with 400 cc. of distilled water. The liquid is boiled for five minutes. Water is added, and the liquid is cooled, shaken, and is filtered upon a folded filter-paper. Of the filtrate 250 cc. are boiled in a porcelain dish, and titrated (neutral litmus-paper as indicator) with N/4 potash that has been standardized under the same conditions with a pure bitartrate. For the analysis of total tartaric acid the method of Goldenberg-Géromont (*Z. anal. Ch.* **37**, 312 (1898)) is usually employed. This method has been studied in detail by the committee. A brief statement is also made concerning the correction to be introduced for the volume of solid material—a subject to be considered in greater detail in a future report.

RECENT WORK IN AGRICULTURAL CHEMISTRY.

Received June 18, 1906.

FERTILIZERS BY F. P. VEITCH.

As usual, numerous experiments have been made for the purpose of determining the relative value of different materials for supplying the essential elements, phosphoric acid, nitrogen and potash.

Only those which are deemed most important need be mentioned here. Haselhoff (*Landw. Jahrb.* **34**, 616–641 (1905)) has conducted a number of experiments to show the value of differently prepared and different mixtures of Thomas slag. Kuhnert (*Mitt. deut. landw. Ges.* **20**, 334 (1905)) has found slag to give better results during the first year than crude ground phosphate. Clausen (*J. landw.* **53**, 213–228 (1905)) has investigated by pot experiments the effect of phosphoric acid on oat plants grown on black peaty sand and has found the total yield to regularly increase while the relative yield of grain was decreased.

In an investigation of the influence of phosphoric acid on wines from grapes, Zacharewicz (*Prog. agr. vit.* (Ed. L' Est) **25**, 459–462 (1904)) finds that phosphoric acid may be accumulated in part in the fruit and contribute beneficially to the wine made from it. Montanari (*Staz. sper. agr. ital.* **38**, 253–258 (1905)), Quartaroli (Abs. in *J. Chem. Soc.* **88**, ii, 549 (1905)), Pervinquiere (*Rev. sci.* **5**, [4] 353–361 (1905)), and Katayama (*Bull. Col. Agr. Tokyo Imp. Univ.* **6**, 353–356 (1905)) have contributed minor papers on phosphoric acid. Haselhoff (*Landw. Jahrb.* **34**, 647–664, pl. 1 (1905)), in extended pot experiments with various potassium fertilizers on potatoes followed by wheat, finds that a partial substitution of potassium chloride by sodium chloride resulted in a slight increase in yield of potatoes but a further increase of sodium chloride gave a decrease in yield. The smallest amount of potash was taken up by potatoes from the kainit. The author concludes that it appears probable that by the application of sodium chloride the potash of a soil is rendered soluble and more easily assimilated by plants.

By treating leucite with various salt solutions, and also with water, Monaca (Abs. in *Centr. agr. Chem.* **34**, 714 (1905)) succeeded in dissolving considerable potash from the finely ground material, such potash being considered assimilable plant food. Reitmair (*Z. landw. Versuchsw. Oesterr.* **8**, 863–944 (1905)) reviews the work of other investigators regarding the conditions under which potash fertilization reduces the protein content of malted barley and concludes that the protein content is only reduced when the quantity of available potash in a soil is at a minimum and is especially reduced on the less fertile soils when a heavy application of nitrogen has been given. Stoklasa (*Z. landw. Versuchsw. Oesterr.* **8**, 957–982 (1905)) presents a reply to the conlcusions drawn by Reitmair on this subject. Vageler (*Vrtljschr. bayer. landw. rat.* **10**, [2] (Ergänzungsh.), Sup. 1, 125–133 (1905)) has examined 143 cultivated Bavarian moor soils and finds that in spite of the fact that they are well supplied with potash they are much benefitted by a liberal application of potash fertilizers. Feilitzen (*Svenska mosskulturför, tidskr.* **19**, 91–100, pls. 4, Fig. 1 (1905)) finds that mangolds and potatoes grown on moor soils frequently show marked need of potash. Prianishnikov (*Ber.*

deut. bot. Ges. **23**, 8–17 (1905)), in reviewing experiments on the effect of ammonium salts on the assimilation of phosphoric acid, concludes that phosphates are rendered more soluble by these salts while sodium nitrate exerts no such effect. Bachmann (*Fühling's landw. Ztg.* **54**, 219–223 (1905)) finds that calcium carbonate applied with sulphate of ammonia increases its action while the action of nitrate of soda is not materially affected by the calcium carbonate. Treboux (*Ber. deut. bot. Ges.* **22**, 570–572 (1904)) has studied the effect of various forms of nitrogen on chlorophyll-bearing plants and finds that nitrites, while generally available in alkaline soils, are poisonous in acid soils. Nitrates and nitrites were found to possess practically the same efficiency while ammonium salts were more available than either. Amines and amides are about equally valuable for the lower plants but amides are less assimilable for the higher chlorophyll-bearing plants. It is claimed that ammonium salts are most suited to the nitrogen nutrition of chlorophyll-bearing plants and that the intervention of nitrite and nitrate bacteria is not always necessary.

The value of calcium cyanamide or lime nitrogen as a nitrogen carrier has received a great deal of attention from European investigators, the following authors contributing to the literature on this subject: Haselhoff (*Landw. Jahrb.* **34**, 597–616 (1905)); von Seelhorst and Müther (Abs. in *J. Chem. Soc.* **90**, ii, 46 (1906)); Immendorff and Thielebein (*Fühling's landw. Ztg.* **54**, 787–795 (1905)); Ashby (*J. agr. sci.* **1**, 358–360 (1905)); Grandeau (*J. agr. Prat.*, N. S., **10**, 808 (1905)); von Feilitzen (*Svenska Mosskulterför. Tidskr.* **19**, 100–110 (1905)); Otto (Abs. in *J. Chem. Soc.* **88**, ii, 196 (1905)); Söderbaum (*Meddel. K. Landtbr. Akad. Exptäjlt.* (Stockholm), No. 85, 27), Löhnis (Abs. in *Chem. Centr.* **1**, 1731); Wein (*Chem. Ztg.* **29**, 1066 (1905)); Grandeau (*J. agr. prat.* N. S. II 8–10 (1906)). Without going into the details of these results, it may be said that in general the experiments have shown that the use of this material upon land on which crops are immediately to be planted, may prove decidedly injurious if large quantities of the material are applied but if the application be made some time before planting the crop, little, if any, injury results. As a nitrogen carrier this material promises to be a valuable addition to our fertilizer materials and to have a value about equal to ammonium sulphate, though this value will differ somewhat with the nature of the soil upon which the material is used.

The formation of nitric acid from the air has continued to occupy a prominent place in the experimental and technical fields and Birkeland and Eyde have devised a process that, according to Witt (*J. Chem. Ind.* **28**, 699 (1905)), is exceedingly promising. The inventors, instead of working with arcs of low amperage, utilize the action of a magnetic field on the arc, by placing powerful electromagnets vertically to the electrodes; the arc formed be-

tween the electrodes is blown away, as it were, by the influence of the magnetic field and at once a new arc is formed which is also blown away. In practice, this formation and removal of the arc takes place several hundred times per second. With 30 kilowatts energy, discs of one metre diameter can be formed. The hollow electrodes are of copper and are cooled internally by water. A yield of 100 grams nitric acid per kilowatt hour is obtained at a cost of about 1 to 2 cents per kilo. The dilute acid is concentrated as much as possible by running the oxides into the solution which is then treated with lime water to form a calcium nitrite which is oxidized to nitrate by treatment with nitric acid. The solution is evaporated and fused, resulting in a basic nitrate which powders readily, and in contact with water, soil and carbon dioxide breaks down into calcium carbonate and nitrate. Schloesing (*Compt. rend.* **141**, 745 (1905)) finds calcium nitrate and nitrite as effective fertilizers as the sodium salts for maize. Bellenoux (*Compt. rend.* **140**, 1190 (1905)) finds calcium nitrate fully as valuable as sodium nitrate in the production of potatoes and sugar beets.

Other papers upon the value of various nitrogenous materials have been contributed by Lutz (*Bull. soc. bot. france*, **52**, 159–162 (1905)); Haselhoff (*Landw. Jahrb.* **34**, 642–646 (1905)); Aumann (Abs. in *Centr. agr. Chem.* **33**, 852 (1904)); Björn-Anderson (*Tidsskr. Landökonom.* 160–168 (1905)); Knecht (*Chem. News*, **91**, 259–261 (1905)); Clausen (*Deut. landw. Presse*, **32**, 611 (1905)); Gerhardt (*Chem. Ztg.* **29**, 194 (1905)); Schäfer (*Fühling's landw. Ztg.* **54**, 142–145 (1905)); Gerlach and Vogel (Abs. in *Chem. Centr.* **1**, 1609 (1905)); Böhme (*Illus. landw. Ztg.* **24**, 1001, 1011, and 1023–1025 (1904)); Boullanger and Massol (*Compt. rend.* **140**, 687–689 (1905)); Lutz (*Compt. rend.* **140**, 380–382 (1905)); Weitz ("Der Chilisalpeter Düngemittel," Berlin: Paul Parey, (1905)); Müller and Spitzer (*Ber.* **38**, 778–782 (1905)); Jamison ("Utilization of Nitrogen in Air by Plants," Report of the Agricultural Research Association of the N. E. Countries of Scotland (1905)) advances the startling doctrine "That plants generally absorb free nitrogen directly from air, and transform it into albumen, that the quantity absorbed and fixed varies according to the number and character of the special structures that perform such function, and to the presence of the conditions of growth necessary to secure development of such structures." It is further stated that neither fungi nor bacteria have the power of fixing free nitrogen but that this power is limited to chlorphyll-bearing plants, and that the seat of fixation is in certain structures of the leaf or stalk. The evidence upon which these conclusions are based is simply the presence of albuminous material in these above-mentioned structures. It is not likely that Jamison's conclusions will be accepted on the evidence submitted. Fisher (*J. Landw.* **53**, 289–297 (1905)) in studying nitrogen-fixing bacteria

has found that the activity of the organisms is greatly influenced by the character of the soil, particularly by its lime content and physical condition. In one soil where the several plots were differently manured only those to which lime has been applied contained *Azotobacter*. Löhnis (*Centr. Bakt.* **13**, 706–715 (1904); 14, 582–604 (1905)) has studied the various nitrifying and denitrifying bacteria and concludes that because soil conditions are as a rule more favorable to nitrification than denitrification, the latter is inconsiderable in well aerated soils. Keutner (*Wiss. Meeresunters, abt. Keil* 8) finds nitrogen-fixing bacteria widely distributed in sea water and in many fresh waters. *A. chroococcum* has the power to fix nitrogen in an 8 per cent. solution of sodium chloride.

The use of lime as an adjunct in agricultural practice is a subject receiving a great deal of attention, and Suzuki (*Bull. Col. Agr. Tokyo Imp. Univ.* **6**, 347–351 (1905)) finds that calcium carbonate decidedly depresses the assimilability of phosphoric acid by rice while calcium sulphate has no such effect. Powdered magnesite also greatly depresses the yield. Loew (*Z. landw. Versuchsw. Oesterr.* **8**, 583–602 (1905)) and Loew and Aso (*Bull. Col. Agr. Tokyo Imp. Univ.* **6**, 335–346 (1905)), in investigations upon the ratio of lime to magnesia, find that this ratio is dependent upon equal availability in the forms in which the lime and magnesia exist, and Loew maintains his well-known views regarding the necessity of having a definite relation between lime and magnesia in the soil in order to insure the highest productiveness. Hoffmann (*Arb. deut. landw. Ges.* No. **106** (1905)) reports in detail a large number of experiments conducted under the auspices of the German Agricultural Society in which the use of lime in rotation experiments proved beneficial in a majority of cases. On light poor soil in dry seasons carbonates proved preferable to caustic lime. Methods for applying different forms of lime are given. Meyer (*Fühling's landw. Ztg.* **54**, 261–267 (1905)), having found that crops grown in zinc pots and fertilized with gypsum gave small yields, has repeated his experiments checking the results with earthenware pots and finds that the yield of leguminous crops is much reduced in zinc pots but that the injury was overcome by adding calcium or magnesium carbonate. Tacke (*Fühling's landw. Ztg.* **54**, 331 (1905)), in referring to the above-mentioned work of Meyer's, calls attention to the earlier work of Fleischer and Tacke and Immendorff with gypsum on acid upland moor soils which indicated that the injury was due to the setting free of acids, and claim this is the explanation for Meyer's results. (This same injury has been observed in the work of the Bureau of Chemistry, U. S. Department of Agriculture, and it should be remembered that zinc sulphate which is undoubtedly formed, is of itself a decidedly acid salt and fully capable of producing all the injury observed, if present in sufficient quantity. Careful ex-

amination renders it doubtful that any quantity of free acid results during the reaction. It seems more plausible, therefore, to attribute the injury to the salt rather than to the free acid. —*Reviewer.*) Hardt (*Deut. landw. Presse*, **32**, 253–254 (1905)) has published results of four years' culture and liming experiments on moor soils. Sutherst (*Chem. News*, **92**, 185 (1905)) proposes to determine the availability of phosphoric acid in 1 per cent. citric acid and finds that the presence of soluble salts modifies considerably the solubility in this reagent. Rippert (*Fühling's landw. Ztg.* **54**, 608–620 (1905)) has reviewed the investigations relating to the fertilizing value of different forms of nitrogen, potash and phosphoric acid and points out that in judging of the efficiency of a fertilizer, a number of different factors such as geographical position, climate, amount of precipitation, geological character of the soil, chemical and physical properties, depth of the surface soil as well as the character of the subsoil must be considered.

Notwithstanding the fact that a great deal of work has been done and that the methods at present for the estimation of fertilizer constituents are in a very good shape, a number of investigators have continued to devote considerable time to improvements in methods with a view of shortening the operation or increasing the accuracy of results. Hissink and Van der Waerden (Abs. *Chem. Centr.* **1**, 1188 (1905)) have so modified the volumetric determination of phosphoric acid as to secure a uniform composition of the yellow precipitate. Hlavnicka (*Z. angew. Chem.* **18**, 655 (1905)) describes a simple modification of Hundeshagen's method, precipitating the magnesium-ammonium phosphate by the citrate method, washing on a hardened filter with $2\frac{1}{2}$ per cent. ammonia and then with alcohol until free from ammonia, the total volume of washing not exceeding 40 cc. The titration is made, using methyl orange as an indicator. Hirt and Steel (*Proc. Soc. Chem. Ind.* Victoria (1905) 14–19, and *Chem. News*, **92**, 113–114 (1905)) slightly modify Littmann's method, which they consider preferable to Pemberton's for commercial work. Raschig (*Z. angew. Chem.* **18**, 374–376 (1905)) shows that the amount of water used in washing magnesium-ammonium phosphate prior to titration may be reduced to 10 cc. Neubauer (*Landw. Vers. Stat.* **63**, 141–149 (1905)) gives a simple method for the determination of phosphoric acid, potash, sodium, calcium and magnesium in hydrochloric acid soil solutions. Schultze (*Chem. Ztg.* **29**, 508 (1905)) estimates calcium oxide and phosphoric acid volumetrically and shortens the regular method for the determination of potash as potassium chlorplatinate.

Schenke (*Landw. Vers. Stat.* **62**, 3–10 (1905)) makes a comparative examination of Märcker's German official citrate method and a modified citrate method for the determination of phosphoric acid in bone meal, Thomas slag and soils. The results

of the modified citrate method agree most closely with the molybdic method. The author points out that the citrate method is a "compensation method." Mach (*Landw. Vers. Stat.* **63**, 81–91 (1905)) finds that the Wagner method and the official German method for determining phosphoric acid agree closely as a rule. The Wagner method gave higher results in slag rich in silica. The Schenke modification of the citrate method gave results that were too high. Seib (*Z. anal. Chem.* **44**, 397–398 (1905)) offers a substitute for the Petermann method as used in Belgium, which shows results agreeing quite closely with the Petermann method. Ledoux (Abs. *J. Chem. Ind.* **24**, 904 (1905)) detects natural phosphates in phosphatic slags by extracting the phosphoric acid of the mixed phosphates with citric acid. This dissolves the phosphoric acid of the slag. The residue is treated with nitric acid and if on adding ammonium molybdate to the solution a precipitate is formed, the presence of natural phosphates is indicated. Svoboda (*Chem. Ztg.* **29**, 453–456 (1905)) has made a critical examination of the Maercker-Bühring solution, Wagner's citrate magnesia mixture, and iron citrate magnesia mixture to show their solvent effect on glass. Boulez (5 *Internat. Kong. angew. Chem. Ber.* **3**, 746–747 (1903)) determines phosphoric acid in the presence of other constituents in phosphatic material by titrating with alkali, using methyl orange and phenolphthalein as indicators.

Järvinen (*Z anal. Chem.* **44**, 333–342 (1905)) determines magnesium in a solution exactly neutralized, using lacmoid as indicator, by the cautious addition of a slightly ammoniacal solution of diammonium phosphate. After standing a short time, 1 per cent. ammonia is added and then 10 per cent. ammonia in quantity equal to one-third the volume of the whole. The determination is made after two hours' standing. Baxter and Griffin (*Am. Ch. J.* **34**, 204–217 (1905)) find that the precipitate of ammonium phosphomolybdate occludes a small amount of molybdic acid which renders the results by this method slightly inaccurate. It is also claimed that 24 molecules of alkali are required for the neutralization of one molecule of ammonium phosphomolybdate and not 23 as commonly assumed. The authors conclude that no method for estimating phosphoric acid which depends upon the determination of the molybdic acid in ammonium phosphomolybdate is accurate unless allowance is made for the occluded ammonium molybdate and molybdic acid. Gerhardt (*Chem. Ztg.* **29**, 178–179 (1905)) determines free phosphoric acid in superphosphates by shaking 20 grams of the superphosphate mixed with 1 gram of ferrocyanide of potassium dissolved in a little water for one-half hour in a liter of water. Filter, add a known weight of calcium carbonate to 100 cc. of the solution and stir for one-half hour. Remove the excess of calcium carbonate by filtering, wash, dry, burn, ignite carefully and weigh.

The difference between the calcium carbonate used and that thus obtained furnishes a means of determining free phosphoric acid. Zöckler (*Chem. Ztg.* **29**, 226–338 (1905)) believes that Gerhardt's method is unreliable and considers the alcohol method safer. Ostersetzer (*Chem. News*, **91**, 215 (1905)) briefly describes the method for using alizarinsulphonic acid as indicator in determining free acid in superphosphates.

Westhausser (*Z. anal. Chem.* **44**, 187–191 (1905)) compares the official German method, the original Kellner-Böttcher method and the Kellner-Böttcher method, using Hallens ammonium citrate solution. All were unreliable on Thomas slags containing large amounts of silica. Alvarez (*Chem. News*, **91**, 146 (1905)) proposes to use sodium aminonaphtholsulphonate for the precipitation of potash in neutral solutions. The precipitate may be washed in alcohol. Ammonium and magnesium salts do not interfere with the reaction. Klinkerfues (*Chem. Ztg.* **29**, 77–78 (1905)) estimates potash by direct evaporation of the water solution with chlorplatinic acid and, after washing the potassium chlorplatinate with a very little water and with alcohol, dissolves it in water in a platinum dish and precipitates metallic platinum by decomposing the salt with formic acid. In a later communication (*Chem. Ztg.* **29**, 1085–1086 (1905)) the author states that it is not necessary to completely dry the salt after the addition of formic acid. This, however, greatly shortens the operation. Pfyl (Abs. in *Analyst*, **30**, 345–346 (1905)) determines nitric acid in the presence of organic substances by reducing nitric acid to nitric oxide by means of ferrous chloride and hydrochloric acid, the nitric acid being washed by passing it through sodium hydroxide solution and absorbing by tenth-normal potassium permanganate solution. The excess of permanganate solution is titrated with tenth-normal ferrous chloride solution. Frerichs (Abs. in *Chem. Centr.* **1**, 957 (1905)) calls attention to the fact that the reaction between nitric acid and diphenylamine is interfered with by the presence of such substances as ferric salts, chromates, etc., and proposes to obviate some of the difficulty by treatment with ether in sulphurous acid solution. Gutbier (*Z. angew. Chem.* **18**, 494–499 (1905)) reports tests of the accuracy of Busch's method for the determination of nitric acid. The Busch method (*Ber.* **38**, 861–866 (1905)) is based on the fact that diphenyleneanilodihydrotriazol forms insoluble compounds with nitric acid and makes it possible to detect this acid in dilutions of 1:60,000 at room temperature, and 1:80,000 at zero temperature. A list of other substances forming similar precipitates which may interfere is given. Tests on pure potassium nitrate show a close agreement with standard methods.

Meisenheimer and Heim (*Ber.* **38**, 3834–3837 (1905)) describe a method for the determination of nitric and nitrous acids based upon the measurement of the nitric oxide set free when nitrous acid

is treated with hydrogen iodide and when nitric acid is treated with ferrous chloride and hydrochloric acid in the usual way. Raschig (*Ber.* **38**, 3911–3914 (1905)) claims priority for the above method. Bensemann (*Z. angew. Chem.* **18**, 939 and 1225–1228 (1905)) proposes a method for the complete analysis of sodium nitrate. Easton (*Chem. Eng.* **1**, 142–145) estimates nitric acid and nitrates by electrolytically reducing to ammonia in a copper solution acidified with sulphuric acid and distilling the ammonia thus formed.

Schloesing (*Compt. rend.* **141**, 745–746 (1905)) has compared the value of calcium nitrate prepared electrolytically with sodium nitrate and a mixture of sodium nitrite and calcium nitrite for the production of corn in pot experiments. All the substances were equally valuable in increasing the yield. Thiele (*Mitt. landw. Inst. Breslau* **3**, 157–178 (1905)) thoroughly reviews the literature relating to the sampling of soils with particular reference to the difficulty of securing representative samples, showing the small differences occurring in plant-food constituents, particularly nitrogen. The results indicate that it is not possible to get a strictly representative sample by present methods of sampling but that it is possible to detect by analysis smaller variations in nitrogen content than are likely to be of significance in experimental work. Trillat and Turchet (*Bull. soc. chim.* [3] **33**, 308–310 (1905)) have examined the nitrogen iodide reaction for determining ammonia in potable waters. They also (*Ibid.* pp. 304–308) propose a new method for determining ammonia which is based upon the fact that when 3 drops of a 10 per cent. potassium iodide solution and 2 drops of a saturated alkali hypochlorite solution are added to 20 or 30 cc. of water containing ammonia, a black coloration is formed. Flamand and Prager (*Ber.* **38**, 559–560 (1905)) modify Kjeldahl's method to make it applicable for the determination of nitrogen in azo-, azoxy-, and hydrazo-compounds. Tschernobajeff (*Chem. Ztg.* **29**, 442–443 (1905)) recommends that chlorates and perchlorates be determined together in sodium nitrate by Lemaitre's method and that chlorates be determined separately by reduction in the cold by means of iron and sulphuric acid according to Hendrixson's method. Bensemann (*Z. angew. Chem.* **18**, 816 (1905)) proposes to reduce nitrate of soda by fusion with oxalic acid until carbonate is formed, and nitrogen and chlorine are expelled.

Soils by F. P. Veitch.

The chemical investigation of soils has continued to receive its full share of attention, and a number of workers have endeavored to establish a relation between crop production and the plant food constituents removed from the soil by various solvents. Marr (*Meded. Proefstat. Oost-Java* [4] No. 4, 65–87) finds that many soils of Java, although containing a low percentage of total

phosphoric acid (less than 0.1), yet produce excellent crops and fail to respond to applications of phosphates. Examination of such soils by the methods of Schloesing and of Dyer (using 2 per cent. citric acid) showed that the former method did not give results agreeing with the crop history of the soil, but that the Dyer method showed the soils to contain sufficient assimilable phosphoric acid. Kudasher (*Zhur. Opintn. Agron.* **6**, 436–437 (1905)) finds in the examination of 62 samples of Chernozem soils that the most fertile soils yield the most phosphoric acid to 0.5 per cent. oxalic acid solution. Ingle (*J. Chem. Soc.* **87**, 43–55 (1905)), from numerous pot experiments with barley, turnips and horse beans, draws the conclusion that while Dyer's 1 per cent. citric acid method measures the relative available plant food in soils at a given time, it does not necessarily show the relative fertility of the soils, as the rapidity with which the available plant food is renewed may differ with the soil. For comparing soils subjected to the same climatic conditions the author deems the method valuable, but does not think that soils from tropical climates may be judged by the standards of temperate climates. This latter thought is also advanced by Couturier (*Bull. assoc. chim. sucr. distill.* **22**, 1302–1304 (1905)). Hubert (*Monit. sci.* [4] **19**, 582–588 (1905)) discusses the value of, and gives methods for the chemical determination of the fertilizer requirements of soil with particular reference to vineyard purposes, and König (*Landw. Vers. Stat.* **61**, 371–396 (1905)) critically discusses the determination of productiveness and plant food requirements of soils from the physical and chemical standpoints. Yegorovo (*Zhur. Opintn. Agron.* **6**, 315–324 (1905)) finds that a 100 volt current of low amperage passed through the soil greatly increases the solubility of phosphoric acid and of ammonia but lowers that of nitric nitrogen.

Methods for the bacteriological examination of soils have received attention at the hands of Löhnis (*Centr. Bakt.* 2te Abt., **14**, 1–9 (1905)) and of Remy (*Fi ith Internat. Kong. angew. Chem.* 784–794 (1903)). Fabricius and von Feilitzen (*Svenska Mosskulturför. Tidskr.* **19**, 84–90 (1905)) find that white moor soils in their natural condition contain but few bacteria, owing to their acid reaction. The bacterial flora is but little changed by drainage but is greatly increased by liming, manuring, admixture of sand and mechanical treatment, and the number of bacteria in a soil is closely related to the temperature, and rises and falls with the latter. It is a well-known fact that soils rich in organic matter are as a rule deficient in available potash, and usually respond readily to applications of potash manures. Recent investigations by Berthelot (*Compt. rend.* **141**, 433–445 (1905)) show that humus materials treated with solutions of potassium or calcium salts form insoluble salts of these metals, thus rendering them of no value to plants. Minssen (*Landw. Vers. Stat.* **62**, 445–476 (1905)) reviews the literature on diffusion in acid and neutral media,

with particular reference to the effect of humus soils. The author concludes from the literature and his own work that no acids in dilute solutions interfere with the diffusion of water or salt solutions [a conclusion diametrically opposed to that which would be drawn from field or pot experiments with lime on acid clay or humus soils. The influence of lime in increasing the permeability of such soils is too well-known to require discussion, and it would seem that the investigator has missed the point of his work.—*Reviewer*].

Of late years the uses to which peat may be put have increased so rapidly that a discussion of the whole subject is opportunely given by Kerr ("Peat and Its Products," Begg, Kennedy and Elden, Glasgow, 1905). Half a century ago the subject of the absorptive power of soils was quite thoroughly investigated. Recently more work has been done along this line by Dittrich (*Z. anorg. Chem.* **47**, 15–162 (1905)), Dusserre (*Chron. agr. vaud.* **18**, 463–466 (1905)) and by Einecke (*Mitt. landw. Inst. Breslau.* **3**, 299–310 (1905)) without developing anything particularly new. It is desirable that attention should be redirected to this line of work as from a more thorough and general knowledge of the subject the behavior and effects of fertilizers may be more fully understood. Dittrich's results showing that calcium chloride solutions exert more solvent effect on potash, lime and soda than ammonium chloride or acetic acid solutions are worthy of mention. The water requirements of plants have continued to receive attention at the hands of von Seelhorst and Müther (*J. landw.* **53**, 239–259 (1905)) who experimented with oats, clover and bare fallow, using pots sunk to the level of the ground, and found that, where the ground was kept cultivated, 256.7 grams of water produced 1 gram of dry matter in oats, while 270.2 grams of water were required on rolled ground. One gram of clover required 423 grams for the first cutting and 1,124 grams of water for the second cutting. It was found that the loss of nitrogen through drainage was greatest under bare fallow. Murinov (*Mater. Izuchen. Russ. Pochv.* No. 16 (1905)) has attempted to determine the effect of the action of earthworms on the chemical composition of the soils, and finds the solubility of phosphoric acid in 10 per cent. hydrochloric acid is increased in all cases, while the quantity of lime gradually increased in the lower layers of the soil and nitrogen was more evenly distributed than at the beginning of the experiment. Stoklasa and Ernest (*Centr. Bakt.* 2^te^ Abt., **14**, 723–736 (1905)) finds that enormous quantities of carbon dioxide, about 130 kilos per hectare per day, during the growing season are set free in the soil chiefly through the action of microorganisms and the roots of higher plants, the former producing slightly the most. The authors are of the opinion that this carbon dioxide converts much plant food into soluble forms,

and that the solvent effect of roots is due to the production of carbon dioxide rather than to the secretion of organic acids.

One of the most valuable, if not the most valuable, contribution to the literature of soils and fertilizers of the year is that of Hall ("The Book of the Rothamsted Experiments," John Murray, London, 1905) who summarizes in a clear and practical way the results of various lines of experiments conducted at Rothamsted for more than half a century. Perhaps the most interesting features, because never brought out before in the papers from Rothamsted, are those tables which bring out the effect of fertilizer residues not only on the yield of crops, but also on the physical condition and chemical reaction of the soil, and also upon the nature of the herbage, the action of bacteria, and the loss of beneficial lime salts in drainage waters. The factors which influence the growth of plants in pots have received attention from Lemmermann (*J. landw.* **53**, 173 (1905)) and also from Voelcker (*Ann. Rep. Chem. Soc. London* **2**, 250–251 (1905)) who think that pot experiments should be conducted in triplicate and repeated before accepting them. Lack of agreement between pot and field experiments is attributed to failure to reproduce in pots actual field conditions.

Geological, mineralogical and chemical investigations of soils have been made by numerous workers to which but mere reference can be made here: "Geological Observations on Analyses of Some West Prussian Soils," by Jentzsch (*Landw. Jahrb.* **34**, 165–176 (1905)); "The Composition of West Prussian Soils," by Schmoeger (*Landw. Jahrb.* **34**, 145–164 (1905)); "Geological Notes on Cocoa Soils," by Cunningham—Craig (*Trinidad Bot. Dept. Bull. Misc. Inform.* 196–200 (1905)); "The Mineralogical Analysis of Soils," by Dumont (*Compt. rend.* **140**, 1111–1113 (1905)); "Classification and Nomenclature of Soils According to Mineralogical Constitution," by Lagatu (*Compt. rend.* **141**, 363–366 (1905)); "Contributions to the Chemical Study of Soils, Waters and Mineral Products of the Region of Chari and Lake Tchad," by Hebert (*Compt. rend.* **140**, 163–165 (1905)); "Soil Investigations in the Philippines," by Sanchez (*Bur. Agr. Rept.* 63–76 (1904)); "Study of Belgian Soils," (*Bull. Agr.* (Brussels) **2**, 85–121 (1905)); "Some Soil Analyses," by Pardy (*Natal. Agr. J. Min. Rec.* **18**, 573–574 (1905)); "Analysis of Spanish Soils" (*Abonos Químicos.* **5**, 25–27 (1905)); "Soils of the Argentine Republic," by Cravetti and by Huergo (*Am. Min. Agr. Argentina, Sec. Agr.* (*Agron*) **1**, 12–59 and 21–65 (1905)); "Soils," by Ingle (*Transvaal Agr. J.* **3**, 731 (1905)); "The Sugar Soils of Jamaica," by Cousins (*Bull. Dept. Agr. Jamaica* **3**, 137–146 (1905)); "The Soils of Montserrat," by Watts and Tempany (*West Indian Bull.* **6**, 263–284 (1905)).

The value of mechanical analysis of soils is considered by Atterberg (*Chem. Ztg.* **29**, 195–198 (1905)), who proposes a new

classification of the different grades of soil particles, and also by Mitscherlich (*Fühling's landw. Ztg.* **54**, 673–675 (1905)) who, while believing that the determination of hygroscopic moisture and of heat evolved on moistening is of no importance from the standpoint of plant growth, thinks that for judging the character of soils mechanical analysis may be replaced by the determination of the heat evolved on moistening or preferably by determining hygroscopicity. Sjollema (*J. landw.* **53**, 67–69, 70–76 (1905)) proposes to isolate colloidal substances by centrifuging the soil and noting the behavior of the colloids with coloring-matters. The value of the determination of loss on ignition is seriously questioned by Mehring (*J. landw.* **53**, 229–257 (1905)), who thinks that the errors of this determination are increased by attempting to restore carbonates by treating with ammonium carbonate. It is claimed that the direct determination of humus by combustion with copper oxide or chromic acid is more reliable and useful than incineration. A number of articles dealing with the estimation of certain soil constituents have appeared during the year, among which may be mentioned papers by Pellet and Tribourg (*Ann. chim. anal.* **10**, 413–416 (1905)); Schultze (*Z. landw. Versuchsn. Oesterr.* **8**, 70–72(1905)); Amos (*J. Agr. Sci.* **1**, 322–326 (1905)); Wohltmann and Schneider (*Chem. Ztg.* **29**, 810–811 (1905)); Sommer (*Deut. landw. Presse*, **32**, 692 (1905)).

WATER BY W. W. SKINNER.

In the examination of mineral waters the phenomenon of radioactivity has attracted much attention. Blanc (*Phil. Mag.* **9**, 148–149) examined numerous samples from Alpine regions and found that most of them produced a certain amount of emanation. In some cases the rate of decay was approximately equal to that of the radium emanation. Some of the deposits, however, produced very little or else a very rapidly decaying emanation, from which the author concludes that the latter are probably due to thorium. The Wiesbaden Thermal Springs were examined by F. Henrich (*Monatsh.* **26**, 149–184) and found to be radioactive. The gases obtained by boiling the waters were radioactive, which phenomenon was much intensified by the removal of the carbon dioxide. The evaporated residue consisting mostly of sodium chloride was found to be only slightly radioactive, but calcium carbonate in the form of aragonite which is deposited from the water at some distance from the spring was found to be strongly radioactive. Mache and Meyer (*Monatsh.* **26**, 595–625) examined some of the mineral springs of Bohemia including Karlsbad, Marienbad and Franzenbad, and found them radioactive. They also found that the rate of decay was about the same as that of radium emanation. The presence of thorium could not be detected. In Karlsbad it was

found that the cold ferruginous spring situated within the thermal belt contained a greater proportion of radium emanation than any of the hot springs. The waters from the St. Joachimsthal mines were also found to be radioactive, and the activity increased with the depth of the source. The lowest spring was found to contain a larger proportion of radioactive emanation than any water heretofore examined. The Gastein Thermal Springs were examined by Mache (*Monatsh.* **26**, 349–372) and found to be radioactive with a rate of decay approximately equal to that of the radium emanation. The active substance was found to be the reissacherite of the deposits from the thermal springs. This mineral nearly equals uranyl nitrate in activity, and contains barium, strontium and calcium, but no uranium. Upon separation the radioactive substance is found along with barium and is presumably radium.

Brown (*J. Chem. Soc.* **87**, 1051) reviews critically the Frankland combustion method, the Wanklyn albuminoid ammonia process and the Tidy permanganate method, pointing out the advantages and disadvantages of each. He believes that neither the Wanklyn nor the oxidation method alone, gives any idea of the source of the organic matter. To correct this he suggests a method by combining the Frankland and Wanklyn methods and by so doing obtains the whole of the carbon and nitrogen of the organic matter, in the form of carbon dioxide and ammonia, determining the quantity of each. The author presents considerable data to substantiate his claims for the method, from which he concludes that the new method is as precise as Kjeldahl's and is more applicable to water, requiring a smaller sample, eliminating the use of sulphuric acid and avoiding all bumping in glass vessels. It also requires less time and attention without sacrificing accuracy.

According to Effront (*Chem. Centr.* **2**, 1253) on the addition of a definite quantity of bleaching-powder, which has been accurately titrated, to a given volume of water, the loss in active chlorine is a measure of the nitrogen of the ammonia and proteids. The diphenylamine reaction for the detection of nitric acid in waters is proposed by G. Frerichs (*Arch. Pharm.* **243**, 80). It is claimed that ferric salts, chromates, etc., do not interfere with the reaction. Franz Utz (*Chem. Ztg.* **29**, 177) proposes an improvement upon the above method of Frerichs by evaporation with hydrochloric acid, claiming that with this modification the method gives results favorably comparable with the methods of Schulze-Tiemann and Mayrhofer. A method for the detection of nitrous and nitric acids by means of diphenylamine is also proposed by Raikow (*Chem. Centr.* **1**, 402). The estimation of ammonia by the method of Trillat and Turchel is claimed by Cavalier (*Bull. soc. chim.* **33**, 745) to be worthless for quantitative work. He believes the method can

be used only after considerable concentration, and even then the nature of the precipitate renders the estimation very difficult. F. Dienert (*Ann. inst. Pasteur*, **19**, 541) discusses various methods and describes in detail a method based upon electric conductivity, which it is claimed is well suited to the study of variations of underground waters. A modification of the Winkler method for determining oxygen in water is proposed by Noll (*Z. angew. Chem.* **28**, 1767) by which more accurate results may be obtained. The purification of water by means of barium carbonate is proposed by Basch (*Chem. Ztg.* **29**, 721). The advantages which are claimed for this procedure are that the permanent and temporary hardness are removed, as well as all the sulphates. This is not the case when caustic lime and sodium carbonate are used for this purpose, one of the results of the latter metathesis being the formation of sodium sulphate which is objectionable for a number of reasons. Calcium peroxide has been proposed by Freyssinge and Roche (*Rev. internat. falsif.* **28**, 49) for the sterilization and purification of drinking-water. It is stated that water can be completely sterilized in about two hours by the addition of 0.4 gram of calcium peroxide per liter.

FEEDING STUFFS BY W. W. SKINNER.

In the proximate analysis of feeding stuffs the attention of investigators is constantly being directed towards that class of substances coming under the caption of nitrogen-free extract, in an effort to more definitely determine the several components of this subdivision. The method of Ellett (Inaug. Diss. Univ. Göttingen 1904) for the quantitative estimation of pentosans and methylpentosans is an instance of this effort. The method proposed is a simultaneous determination of methylpentosans and pentosans in vegetable products. He confirms Votocek's statement that methylfurfural phloroglucide, even when dried, is soluble in alcohol, while furfural phloroglucide is not. Upon this fact he bases his method by obtaining the two together and weighing, and then dissolving out with alcohol the methylfurfural phloroglucide and again weighing. Details of the method are given and the data offered indicate that the method, as worked out, gives satisfactory results. V. Storch (*Ber. Vet. Land. Lab. Landökonom.* **58**, 180) explains in detail the methods employed in the analysis of feeding stuffs by the chemical department of the Copenhagen Experiment Station. The faults of the conventional methods for determining nitrogenous components, crude fiber, and nitrogen-free extract are pointed out and discussed. The author recommends that the following determinations be made, *viz.*, fat, albuminoids, sugar, starch, pentosans, ash, and water, with cellulose and other undeterminable substances grouped by difference. This scheme is now employed at the Copenhagen Station. J. König (*Internat. Kong. angew. Chem.*

5, 1052) describes his method for the determination of crude fiber in foods and feeding stuffs by means of a mixture of glycerol and sulphuric acid. The amount of lignin in the crude fiber is determined by hydrogen peroxide and ammonia, which dissolves the lignin, leaving the pure cellulose. An exhaustive study of the value of sorghum seed as a feeding stuff has been made by Tangl, Weiser and Zartschek (*Landw. Jahrb.* **34**, 3–64). The authors experimented with horses, steers, cows, sheep, pigs and poultry, and in addition to studying the digestibility of the seed, the income and outgo of nitrogen were determined. From their work they consider sorghum seed a valuable feed, but that to attain the best results it should be mixed with some other grain. Especially is this true for horses.

CEREALS BY J. S. CHAMBERLAIN.

One of the important contributions of the year to the chemistry of cereals is the monograph by F. F. Bruyning, Jr., ("La valeur boulangere du froment," Archives Teyler [II], **9**, Parts 3-4, Haarlem (1905)) on the baking value of wheat. It is a book of 217 pages and its object is to give a view of the actual state of our knowledge of the baking properties of different kinds of wheat, especially from the point of view of the milling and baking industries of Holland. E. Fleurent has published under different titles (*Ann. chim. anal.* **10**, 129, 195, 238, 276 and 309 (1905), (*Compt. rend.* 140, 99 (1905)) a resumé of his work for several years on the determination of gluten. He draws the following conclusions: (1) Wheat gluten is a definite substance and its mechanical extraction, if carried out under proper conditions, is definite and exact. (2) Distilled water and water containing calcium chloride or sulphate or sodium chloride cause a loss in the determination of gluten, but this loss is lessened if calcium bicarbonate is present. (3) In determining gluten only the soluble proteids are lost in the washing and not the gluten. If calcium chloride or sulphate is present in the wash-water the amount of gluten lost is proportional to the amount of globulin present. (4) Prolonged washing causes a loss in gluten and the gluten so lost always contains gliadin and glutenin in the proportion of 75:25. (5) The acidity of old flours tends to lessen the ease of washing out the gluten but neutralization of the excess acidity by means of sodium bicarbonate makes the determination satisfactory. (6) Allowing the mixed dough to stand before washing tends to loss of gluten. (7) The amounts of gluten extracted at temperatures between 15° C. and 35° C. are practically the same. (8) Water at 16° C. containing 80–90 mg. of salts per liter, of which 80–90 per cent. is in the form of calcium bicarbonate, is the best for washing out gluten. The washing should take ten to eleven minutes and the final washing two to three minutes. The gluten should be dried at 105° C. Results should

agree within 0.20 per cent. The influence of the constituents of brown or low-grade flour on the determination of gluten has been examined by Lindet and Amman (*Compt. rend.* **141**, 56 (1905)) who find that among other things there is present in dark flour a mucilaginous substance which prevents the gluten from adhering together as usual. A determination of the hydrolytic cleavage products of the protein "gliadin" by means of dilute acid has been made by E. Abderhalden and F. Sammely (*Z. physiol. Chem.* **44**, 276 (1905)). They find, as did Osborne and Harris (*Am. J. Physiol.* **13**, 35 (1905)) by practically the same method, that by far the greatest part of the cleavage products obtained is in the form of glutamic acid. They find 31.5 per cent. of glutamic acid while Osborne and Harris found 37 per cent. Also that gliadin yields none of the diamino acid lysine and therefore differs sharply from the alcohol-insoluble protein gluten casein (glutenin) which yields a considerable quantity. The amino compounds obtained as cleavage products of gliadin are as follows: Glycocoll, 0.68 per cent., alanine, 2.66 per cent.; aminovaleric acid, 0.33 per cent.; *a*-proline, 2.40 per cent.; leucine 6.00 per cent.; glutamic acid, 27.60 per cent.; aspartic acid, 1.24 per cent.; phenylalanine, 2.60 per cent.; serine, 0.12 per cent.; tyrosine, 2.37 per cent.; tryptophane, 1.00 per cent.

Chapus (*Bull. Agr. Algerie et Tunis*, No. 7, 11 (1905)) discusses the views held and advanced especially by Fleurent and Balland in regard to the differences in composition between hard wheats and soft wheats, the relation of protein content to yield, the determination of gluten and the significance of the proteins gliadin and glutenin. Physiological experiments with man and the nutritive value of different kinds of flour have been made by P. Fauvel (*Compt. rend.* **140**, 1424 (1905)), who finds, from results obtained using white flour, whole wheat flour and brown army flour, that whole wheat bread, though containing more than twice as much phosphoric acid as the army bread, yet does not yield as much assimilable phosphoric acid as the latter. The whole wheat bread diminished the excretion of urea and produced an appreciable quantity of purine bodies. It also irritated the intestines and diminished the assimilation of other nutrients. The army bread was superior to the white and possessed none of the undesirable properties of the whole wheat bread. A case of poisonous flour made from rye infested with a fungus, *Fusarium roseum*, was reported by A. Yachevski (*Russ. J. exp. landw.* **6**, 249 (1905)).

Work on barley and malt has been carried on by several investigators. Vanha, Kyas and Bukovansky (*Ztg. landw. Versuchsw. Oesterr.* 667 (1905)) have demonstrated that seed of high nitrogen-free extract, low total protein and high soluble protein content gave a crop of increased total yield, an increase in yield of grain, number and weight of stalks and total weight of heads. This

influence is explained by the fact that the nitrogen-free extract acts as reserve material and that the best developed embryo is found in seed of high nitrogen-free extract. They conclude that neither nitrogen-free extract nor protein content are transmitted characters but depend chiefly on the quality of soil and the supply of plant food. Other investigations on the relation between protein content and yield have been made by Schneidewind (*Wochenschr. Brau.* **22**, 29 (1905)), who maintains that with barley as with other plants the higher the yield under like conditions the lower the protein content. He claims that this is explained by the fact that in the first and middle period of growth large amounts of nitrogen are assimilated and if growth is then suddenly checked the formation of starch is hindered and the nitrogen content will be high. The bettering of the quality of barley by a mechanical and chemical study of the composition of barley soils has been undertaken by J. Stoklasa (*Chem. Centr.* 1905, I, 761). According to the author the rôle of potash in starch formation is such that the amount of potash assimilated stands in a constant ratio to the amount of starch in the grain. One gram assimilated potash produces 23 to 25 grams of starch. The best brewing barleys and their relation to crop rotation and fertilizers have been investigated by E. Schribeaux (*Ann. brass. dist.* **8**, 185 (1905)), and the abnormal character of the barley of the crop of 1904 and beer produced from it has been studied by W. Windisch (*Wochenschr. Brau.* **22**, 373 (1905)). The turbidity of the "White" beers obtained may be due either to abnormal albuminoid bodies or to abnormal carbohydrates such as pectins. If due to albuminoid bodies they must be compounds intermediate between albumins and albumoses.

A modification of Lindet's method for the examination of malt has been published by Ford and Guthrie (*J. Inst. Brew.* (London) **11**, 206 and 326 (1905)). A study of methods for the ash determination of malt has been made by W. Windisch (*Wochenschr. Brau.* **22**, 17 (1905)). The enzymes of malt have been investigated by W. Issajew (*Z. physiol. Chem.* **45**, 331 (1905)), who concludes that there is present in barley and malt a substance possessing all the properties of an oxydase. The ease with which it accelerates oxidation, its relation to temperature and toward reagents, its "Spezifität," etc., all serve to show its enzymic nature. Its rôle in various physiological processes, especially in germination, is doubtless very important. J. Effront (*Compt. rend.* **141**, 626 (1905)) finds that during germination of malt the saccharifying power and the liquefying power of diastase are developed unequally. The saccharifying power increases irregularly and after having attained its maximum diminishes gradually. The development of the liquefying power is slower but more regular and on reaching its maximum it is maintained for some time. When germination is produced in sunlight the difference in the develop-

ment of the two powers is very marked. These phenomena evidently have a direct relation to the transient formation of acid amides during germination. The action of chemical agents on the germination of barley is very complex. Phosphates, lime water and copper sulphate favor germination. Xylene acts favorably toward both saccharifying power and liquefying power. Ammonium chloride increases the liquefying power. Lactic acid, vegetable peptone and neutral calcium hypochlorite increase germination and both enzymic activities but if the calcium hypochlorite is alkaline, it favors germination but weakens the diastatic power.

A study of the value of different sized kernels of rye for baking and feeding purposes has been made by Bastecky (*Chem. Centr.* 1905, I, 465). The influence of soil moisture on the composition of oats has been investigated by Seelhorst and Fresenius (*J. Landw.* **53**, 21 (1905). Their conclusions from pot experiments are: Straw grown on dry soil is characterized by a high digestible protein content. The albuminoid nitrogen diminishes less with increasing moisture content of soil than do the total nitrogenous bodies. The digestible protein diminishes more rapidly than the total protein. The increase in ash and organic matter during the growth of oats has been examined by M'lle Stefanowska (*Compt. rend.* **140**, 58 (1905)). The curves representing the increase in fresh substance, dry substance and ash all have a similar character, increasing slowly per day of growth at first and during maturity increasing very rapidly. The same is true of organic nitrogen, phosphoric acid, lime, potash and iron. An important contribution to our knowledge of the chemical composition and nutritive value of sorghum seed and oats is that by F. Tangl, of the Experiment Station for Animal Physiology of Budapest, and his associates (*Landw. Jahrb.* [3] **34**, 65 (1905)). The coefficients of digestibility of sorghum on steers, sheep, horses and swine, and of oats on horses and sheep are given for each constituent. The average composition and nutritive value of both feeds are also given in numerous tables. They calculate the physiological nutritive value of oats fed to horses as 54.80 per cent., with sheep 53.85 per cent. Sorghum grain alone is not a satisfactory feed for horses, but if fed with twice its weight of oats, it is good. Becquerel (*Compt. rend.* **140**, 1652 (1905)) has shown that the effect of low temperature upon the vitality of various leguminous and cereal seeds depends upon the amount of water and gas present in the seeds. As the result of experimental work Dumont (*Compt. rend.* **141**, 686 (1905)) concludes that the rays of light which act the most effectively upon the migration of albuminoids in grain are those which have the least effect on the chlorophyll function, *viz.*, dark brown, green, blue, red, in the order given. The aleurone grains found in cereals and other seeds have been studied by S. Posternak (*Compt. rend.* **140**, 322 (1905)). The aleurone

grains are formed during the maturity of the seed when the kernel is drying out. The common conception that the aleurone grains are reserve nitrogenous material of the seed is not in accord with the facts. About 50 to 75 per cent. of the aleurone grains are proteid material, but the 25 to 50 per cent. of the non-proteid materials play an important part in the life of the embryo plant. The author finds a new organic phosphorus compound, *viz.*, anhydrooxymethylene diphosphoric acid or "phytin" and also an organic acid yielding a reducing sugar by hydrolysis. An elementary analysis of aleurone grains from various seeds shows that they contain a considerable quantity of all those mineral elements considered indispensable to the development of a plant. The author claims, therefore, that the aleurone grains are not simply a source of reserve nitrogenous material, but that they are a complete mineral food for the embryo plant, and that the mineral elements are present in the seed, as in the case of phosphorus cited above, in organic combination.

For the detection of sawdust in flour Paganini (*Chem. Ztg. Rep.* **23** (1905)) recommends the addition, to a thin layer of the flour, of a few drops of a 20 per cent. aqueous solution of phenylendiamine followed by a few drops of acetic acid. A bright yellowish red color is formed in the presence of sawdust. The reagent is claimed to be much more delicate than phloroglucin and hydrochloric acid. In the examination of noodles and other edible pastes, Filsinger (*Z. öffentl. Chem.* **11**, 332) and Lührig (*Z. Nahr.- Genuss.* **10**, 153 (1905)) suggest the determination of lecithin. Phosphoric acid does not afford sufficient data for judging of the nutritive value of noodles. A fairly complete proximate analysis is suggested as well as the determination of digestibility.

FOODS BY W. D. BIGELOW.

Spices, Etc.—Jaeger (*Z. Unters. Nahr.- Genuss.* **10**, 761–762 (1905)) has discussed at considerable length methods for the detection of cocoa shells in spices. The literature of the subject is reviewed. The presence of reducing sugar in mace has afforded the opportunity, which has not been neglected, of adulterating the product with sugar. Ludwig and Haupt (*Z. Unter. Nahr.- Genuss.* **9**, 200–204 (1905)) examined a series of samples of mace and found a dextrorotary reducing sugar, the amount present varying from 1.65 to 4.28 per cent. Windisch (*Oesterr. landw. Vers. Wes.* **8**, 74) has continued his study of the ash of paprika, and has compared the results of a microscopic analysis with the chemical results on the content of ash and sand in the samples. His former conclusions are confirmed. A high content of sand is regarded as sufficient ground for condemnation. Süss (*Pharm. C. H.* **46**, 159) calls attention to the custom in the retail trade of selling underground pimento superficially colored with ochre, or

similar bodies. The adulteration can frequently be detected by a lens as well as by the examination of the ash. For the determination of artificial coloring-matter in prepared mustard and powdered mustard, the same writer (*Pharm. C. H.* **46**, 291) shakes 50 grams of the sample with 75 cc. of 70 per cent. alcohol, filters, and makes the ordinary dyeing tests. In case the wool does not take on a marked color which is altered by either ammonia or hydrochloric acid, he concludes that no artificial coloring-matter has been employed. Filter-paper is also dipped into the solution, dried, and tested with hydrochloric acid and ammonia.

Coffee and Cocoa Preparations.—The soluble glaze on 32 samples of roasted coffee was examined by Orth (*Z. Unters. Nahr.- Genuss.* **9**, 137 (1905)) according to the method suggested by Hilger. He finds that candied coffee produced by roasting with the addition of sugar, and so distinguished from ordinary glazed coffee, contains from 5 to 7.7 per cent. of soluble material. The standard of 4 per cent. that has been suggested as a maximum will thus not apply to candied coffee. Ottolenghi (*Atti della r. accademia dei fisiocritici* [4], **15**, (1903) 11 pp. Reprint) calls attention to the frequent use of the seeds of *Astragalus boeticus*, and suggests the microscopic detection of the latter in the portion of the sample that sinks to the bottom of water. Balland (*J. pharm. chim.* [6] **20**, 543–549 (1904)) and Puckner (*Pharm. rev.* **23**, 305–309 (1905)) discuss the determination of caffein. A study of the chemical and microscopical nature of coffee substitutes prepared from unmalted and malted grain has been published by Prillach (*Z. Unters. Nahr.- Genuss.* **10**, 118 (1905)). Filsinger (*Z. öffentl. Chem.* **11**, 8–10 (1905)) discusses the composition of "soluble" cocoa, and directs that the soluble alkalinity must be determined and not the total alkalinity, which gives too high results. The same subject is discussed by Fröhner and Lührig (*Z. Unters. Nahr.-Genuss.* **9**, 257 (1905)) and by Lührig (*Z. Unters. Nahr.- Genuss.* **9**, 267 (1905)). According to Kuhl (*Pharm. Ztg.* 631 (1905)) the microscopic examination is valueless for determining the variety of cocoa beans employed, or the presence of an excessive amount of cocoa shells. Quantitative examination alone can determine the latter point.

Vegetables.—Frerichs and Rodenberg (*Arch. Pharm.* **243**, 675–683 (1905)) give the results of the examination of peas at various stages of their maturity, and of canned peas, and discuss the application of the results to the inspection of the product. Riess (*Arbb. kais. Ges. A.* **22**, 663–666 (1905)) has investigated the compound formed by the action of copper salts in the greening of peas, and methods for the detection of copper. He suggests that copper may be determined by macerating with water, strongly acidifying with hydrochloric acid, and separating by means of iron. The result of the examination of frozen potatoes has been given by Parow (*Z. Spiritusind.* **28**, 405 (1905)). Wintgen (*Z. Unters.*

Nahr.-Genuss. **10**, 757–761 (1905)) has reported an interesting case of the swelling of canned goods without any appearance of decomposition. The examination of samples shows the excessive gas to consist largely of hydrogen, and masses of a dark colored product which proved to be chiefly phosphate of iron were found in patches at the side of the receptacle. The author concluded that the nature of the sample was due to the action of the acid upon the imperfectly plated iron, an iron salt being formed with the elimination of hydrogen.

Fruit Products.—The year has been marked by a largely increased number of analyses of fruit products of various descriptions for the purpose of securing data for the establishment of standards. A. Beythien (*Z. Unters. Nahr.-Genuss.* **10**, 339 (1905)) has studied the relation between the composition of fruit juices and the alkalinity of their ash. He confirms the earlier belief that the ratio of ash to alkalinity lies between 1 to 10 and 1 to 15, rather than in the neighborhood of 1 to 5.3 as has been said by Evers. A method for the preparation of fruit juices and standards of composition have been adopted by the association of German food manufacturers and dealers (*Pharm. Ztg.* 380 (1905)). A. and M. Dominikiewicz (*Z. Unters. Nahr.-Genuss.* **10**, 735–744 (1905)) called attention to the relation between viscosity and refractive index of fruit juices and fruit sirups. They believe that the determination of vicsosity and index of refraction are sufficient for the examination of these products with reference to their purity. Otto and Tolmacz (*Z. Unters. Nahr.-Genuss.* **9**, 267 (1905)) find the unfermented beverages on the market to be grossly adulterated. Some are prepared from dried fruit and others are entirely artificial. Further studies regarding the normal composition of fruit juices and standards for the same have been conducted, especial attention having been given to raspberry juice. Complete analyses have been made of the products of 1905 of the various localities prepared in a different manner. The results published are of great value for the establishments of standards for the inspection of fruit products. Among the chief contributors are P. Buttenberg (*Z. Unters. Nahr.-Genuss.* **9**, 141–145 (1905)); F. Morschöck (*Z. Unters. Nahr.-Genuss.* **10**, 733–735 (1905)); E. Baier (*Z. Unters. Nahr.-Genuss.* **10**, 731–732 (1905)); A. Juckenack (*Z. Unters. Nahr.-Genuss.* **10**, 729–730 (1905)); A. Beythien and L. Waters (*Z. Unters.-Nahr.-Genuss.* **10**, 726–729 (1905)); H. Lührig (*Z. Unters. Nahr.-Genuss.* **10**, 714–726 (1905)).

Wine.—Windisch and Roettgen (*Z. Unters. Nahr.-Genuss.* **9**, 70–81 (1905)) have published a systematic review of the methods for the determination of volatile acids. They call attention to the fact that the arbitrary method commonly employed for this determination gives incomplete results because of insufficient distillation. They recommend that the distillate be increased

to 300 cc. They also call attention to the fact that lactic acid passes over with steam with some difficulty, and discuss its influence on the determination of volatile acids in wine. The same authors (*Z. Unters. Nahr.- Genuss.* **9**, 129–133 (1905)) studied the changes in composition of wine occasioned by the use of different clarifying agents. They conclude that the composition of wine is only slightly modified, especially in the case of isinglass and gelatin. Beneschoosky (*Z. landw. Versuchsw. Osterr.* **8**, 78–82 (1905)) called attention to the high volatile acid content of Italian wines. Out of 30 samples examined from various districts in Italy, 12 contained less than 0.1 per cent. of volatile acids, and 18 between 0.1 and 0.3 per cent. Of 913 samples of German wines examined 90 per cent. varied within the limits of 0.01 and 0.069 per cent. The amount of succinic acid in 15 samples of Italian wines is reported by Prandi (*Staz. sper. agr. ital.* **38**, 503) as from 0.0820 to 1.1103 per cent. In the majority of cases it varied from 0.03 to 0.13 per cent. Krug (*Z. Unters. Nahr.- Genuss.* **10**, 417 (1905)) determined the sodium content in a series of samples of wine. The maximum content found was 6 mg. In over 80 per cent. of the samples examined less than 1 per cent. of sodium was found. According to Partheil (*Fifth Internat. Kong. angew. Chem. Ber.* **3**, 1019–1022 (1903)) the usual method for the determination of lactic acid in wine neglects the fact that acid is volatile with steam. He suggests the precipitation of tartaric, citric, and succinic acids with barium salts. Lactic and acetic acids may be distilled from the filtrate with steam. Pairault (*Bol. Cámara Com. Asunción, Paraguay* [15] (1904)) has studied the manufacture of orange wine. As ordinarily conducted the fermentation is slow because of the absence of sufficient materials for the nutrition of the yeast cells. The writer suggests the addition of sugar and mineral salts. Kramszky (*Z. Unters. Nahr.- Genuss.* **10**, 671 (1905)) has reported the composition of raisins and discussed the same with reference to the manufacture of raisin wine. Ruff and Jeroch (*Chem. Ztg. rep.* 74, 1905) calls attention to incomplete results obtained in the direct titration of sulphurous acid, owing to the oxidation of sulphites by the oxygen of the air.

Distilled Liquors.—Schidrowitz (*J. Chem. Ind.* **24**, 176–178 (1905)) discusses standards proposed for the composition of distilled liquor. He suggests as suitable maximum standards 40 mg. of total acids (calculated as sulphuric acid), 0.3 gram of fusel oil, and 0.25 gram for extract. A board of control and rigid inspection are suggested. The manufacture of alcohol from grape pomace is suggested by Perkins and Jamieson (*J. Dept. Agr. So. Aust.* **9**, 24–38 (1905)). It is stated that the pomace should give about 32 gallons of proof spirit per ton, 80 per cent. of which may be recovered by leaching and fermenting. The methods of manufacturing brandy from various fruits are

discussed by Windisch (*Deutsche Essigindustrie* **9**, 89–91 (1905)) and Kayser and Dienert (*Ann. science agron.* [2] **10**, 209–219 (1905)). A study of the bacterial action that occurs during the fermentation is included. Contributions to the literature of the examination of distilled liquors have been made by Hehner (*Analyst*, **30**, 36–56 (1905)), Rocques (*Ann. chim. anal.* **10**, 103–108 (1905)), Beckmann (*Z. Unters. Nahr.- Genuss.* **10**, 143–152 (1905)) and others.

Vinegar. — Jonscher (*Z. öffentl. Chem.* **11**, 467–473 (1905)) discusses standards for wine vinegar. He believes that little can be accomplished by analytical data. Froehner (*Z. Unters. Nahr.- Genuss.* **9**, 361–363 (1905)) considers lactic acid as a normal constituent of wine vinegar, and suggests that the amount of that substance present may be of value in judging the quality of the product. For the same purpose Fresenius (*Z. Unters. Nahr.- Genuss.* **10**, 121–129 (1905)) and Möslinger (*Z. Unters. Nahr.- Genuss.* **10**, 125 (1905)) suggest the determination of glycerol. The amount of glycerol in wine is not reduced in the manufacture of vinegar. Maustbaum (*Revista chim. pura app.* 1905, p. 8) suggests the detection in wine vinegar of acetic acid made by the distillation of wood by means of the furfural reaction and the reduction of permanganate. The latter is believed to be the better of the two methods.

Preservatives.—An unusual amount of attention was given during the year to the question of detecting preservatives in food. The tendency to the quantitative detection is very noticeable. Considerable attention has been paid to the effect of preservatives on nutrition and health, and on the whole the tendency of hygienists is evidently more adverse to the use of preservatives than formerly. During the last year the subject of the determination of boric acid has proved an interesting field of work to a large number of men. The literature of the quantitative determination of boric acid has been thoroughly reviewed by Windisch (*Z. Unters. Nahr.- Genuss.* **9**, 641–660 (1905)) who suggests the elimination of the difficulty occasioned by the use of two indicators with the consequent error, owing to the presence of traces of phosphoric acid that cannot be removed. He proposes the neutralization of the solution by means of iodine and thiosulphate solution, according to Jones, and the titration of the boric acid (which is then free) with phenolphthalein as indicator. (The results of the method outlined by him, however, have not met with general satisfaction at the hands of other workers.—*Reviewer.*) Fritzsche (*Apoth. Ztg.* **20**, 856 (1905)) believes that a positive reaction for boric acid by the turmeric paper test is sufficient for the condemnation of the sample, and that negative results may readily be obtained in the absence of boric acid by the use of pure reagents. Fendler (*Apoth. Ztg.* **20**, 868 (1905)) called attention to the fact that boric acid may be detected in a solution con-

taining 0.005 per cent., and suggests that it should only be reported as present when a strong reaction is obtained. He believes that traces may occur in normal meat, or result from the salt employed in packing it (see this Journal, **28**). He suggests (*Apoth. Ztg.* **20**, 757 (1905)) that the best results are given by a solution containing 10 per cent. of hydrochloric acid, and suggests a 10 per cent. solution of ammonia for the confirmatory test. He proposes the preparation of turmeric paper by immersing strips of turmeric paper in a solution of 0.05 gram of curcumin in 100 cc. of absolute alcohol, and drying in the dark. He calls attention to the fact that the flame test is not nearly so delicate as the turmeric paper test. He suggests that where an evident flame test is obtained it is sufficient without confirmation, but states that this test is not without objection because of its subjective nature. He also suggests that in place of turmeric, safflower and marigold may be used as boric acid reagents. Goske (*Z. Unters. Nahr.-Genuss.* **10**, 242–243 (1905)) suggests the method for the detection of boric acid which was originally proposed by Howard (*Science* **19**, 583 (1904)) for the detection of curcumin. He states that by this method boric acid may be detected in solutions varying from 0.001 to 0.0001 per cent. (This method has also been employed by Bigelow and Brinton for the quantitative determination of boric acid.) Mezger (*Z. Unters. Nahr.-Genuss.* **10**, 243–245 (1905)) proposes a modification of the flame test for boric acid. He adds to the ash in a flask 2 cc. of strong hydrochloric acid, and from 15 to 20 cc. of methyl alcohol. The flask is then attached to a reflux condenser and heated on a water-bath at least 70° for one-quarter of an hour. If hydrogen be passed through the mixture after cooling, the boric acid compound is carried with it, and may be detected by the color of the flame. O. von Spindler (*Z. Unters. Nahr.-Genuss.* **10**, 478–482 (1905)) reviews the literature on the determination of boric acid and proposes a new apparatus for the flame test. Blarez (*Chem. News* 1905, p. 39) has proposed a modification of the method ordinarily employed for the detection of fluorides in wine. He finds they may be more completely precipitated by barium salts than by calcium salts, and suggests the addition of barium acetate after adding a small amount of soluble sulphates. The precipitate is settled by centrifuging, separated by filtration, and ashed, after which the usual method is employed. The influence of formaldehyde on fermentation has been studied by Hirsch (*Allgem. Z. Bierbrauerei Malzfabrik.* 1905, Aug.) and new methods for the detection of formaldehyde, or modifications of old methods have been proposed by Lyons (*Pharm. J.* **75**, 443 (1905)), Voisenet (*Bull. soc. chim.* **33**, 1198–1214 (1905)) and Nicolas (*Compt. rend.* **58**, 697–698 (1905)). The last-named suggests that the greenish fluorescence obtained in milk containing formaldehyde by the addition of amidol will permit the

recognition of the preservative in quantities of 1 to 500,000, or less. Before applying the reagent the milk is clarified with acid, and the filtrate is employed. Schuch (*Z. landw. Versuchw. Oesterr.* **8**, 1058–1060 (1905)) made a comparative study of methods for the detection of formaldehyde and gave his preference to that of Arnold and Mentzel. Considerable attention has been given during the year to the use of hydrogen peroxide as a preservative. The literature of the subject has been reviewed by Lukin (*Centr. Bakt.* **15**, 20–32 and 165–174 (1905)). E. von Mahler (*Chem. Ztg.* **29**, 32 (1905)) proposes the detection of saccharin by fusing the residue from the ether extract with sodium or potassium, extracting the sulphide so prepared from the charred mass by means of water and pouring the solution into a solution of sodium nitroprusside. The red-violet color so obtained is a certain indication of the presence of saccharin since no other compound containing sulphur and soluble in ether is present in food. Grimaldi (*Staz. sperim. agron. ital.* **38**, 618 (1905)) gives the results of the quantitative determination of salicylic acid in several fruits, and a partial review of the literature relating to the distribution of salicylic acid in nature. The disappearance of sulphurous acid in wine is discussed by Carles (*Rep. Pharm.* [3] **17**, 97–102 (1905)). Methods for the determination of sulphurous acid in foods were compared by Schumacher and Feder (*Z. Unters. Nahr.-Genuss.* **10**, 649–659 (1905)). The ordinary method of distillation was found to give satisfactory results. The suggestion that the results obtained by the method are influenced by the sulphur content of illuminating gas used in the operation was put to a severe test. It was found that no inaccuracy was occasioned by the gas burned in the room in which the operation was conducted.

Meat Products.—The methods for the determination of saltpeter in meat preparations have been studied by E. Crespolani (*Bull. chim. farm.* **44**, 697–700 (1905)), K. Farnsteiner (*Z. Unters. Nahr.-Genuss.* **10**, 329 (1905)), and W. Stüber (*Z. Unters. Nahr.-Genuss.* **10**, 330 (1905)). It has been shown that when 1 gram of potassium nitrate is added to 300 grams of meat it is reduced first to nitrite and then to ammonia. The Ulsch method was found to be entirely unreliable for the determination of potassium nitrate because of the effect of the reagents on proteids. By the Schlösing-Wagner method from 99.58 to 102 per cent. of the nitrate present was recovered. E. Carlinfanti and A. Manetti (*Archivio di farmacol. sperim. scienze affini*, **4**, heft 7–8) made a systematic examination of canned meats for the Italian army. They regard canned meat as less digestible than fresh meat and explain the repugnance that has been experienced after a continuous diet of canned meat to its large fat content. Ground cereal products have been reported by H. Matthes (*Z. Unters. Nahr.-Genuss.* **9**, 732 (1905)) as adulterants for corned beef. M. Toyonaga (*Bull. Col.*

Agr. Tokyo Imp. Univ. **6**, 89–95 (1904)) has summarized the results of other investigators with reference to the calcium content in the different animal tissues, and discussed its relation to magnesium. Klikton (*Z. Unters. Nahr.- Genuss.* **10**, 159 (1905)) has investigated the number of errors in the determination of sulphites in meat, owing to the sulphur content of the gas employed. He finds that in a room of 109 cubic meters no appreciable amount of sulphurous acid could be detected after nine gas burners had been employed for ten hours.

Meat Extract.—M. Siegfried and E. Singewald (*Z. Unters. Nahr.- Genuss.* **10**, 521–527 (1905)) pointed out that the deterioration of meat extract is accompanied by the conversion of organic phosphorus into the inorganic form. After a series of analyses of extracts of known origin they suggest that the quality and age of an extract may be judged by estimating the total phosphorus and organic phosphorus. K. Micko (*Z. Unters. Nahr.- Genuss.* **10**, 393 (1905)) has applied Fischer's ester method of hydrolyzation to the determination of the presence of polypeptids in meat extracts. Kutscher (*Centr. physiol.* **19**, 504 (1905)) has made a careful study of the various meat bases in meat extract. He concludes that such products do not have a uniform composition and bodies are sometimes found in it which are not necessarily constituents of muscular tissue. He identified ignotine, methylguanidine, carnomuscarine, neosine, novaine, and oblitine. Barral (*J. pharm. chim.* [6] **22**, 392–395 (1905)) reports the analysis of a so-called papayin meat powder.

Separation of Proteids.—H. C. Haslam (*J. Physiol.* **32**, 267–298 (1905)) has suggested new methods for the separation of proteid bodies which he regards as more exact than those commonly employed. He believes that the methods now in use afford results that are far from satisfactory, owing to the tenacity with which the various proteid bodies cling to each other. This tenacity he explains by the supposition that a loose chemical composition exists among them resulting in chemical equilibrium, which is upset by the addition of a precipitant with the result that only a partial separation is effected, some of the soluble proteids going into the precipitate, and some of the insoluble proteids remaining in the filtrate. Important contributions to the literature on the hydrolysis of proteids and the cleavage compounds formed have been made by Z. H. Skraup (*Monatsh. Chem.* **26**, 243–264 (1905)), A. Kossel and Dakin (*München. Med. Wochnschr.* **51**, 545 (1904)), F. Dubrowin (*Inaug. Diss.* St. Petersburg, 1902), and Hayashi (*Arch. Expt. Path. Pharmakol.* **52**, 289 (1905)). R. Steinegger (*Landw. Jahrb. Schweiz*, **19**, 512–527 and 528–529 (1905)) has studied the influence of formaldehyde on casein and other proteid bodies. The increased acidity caused by the addition of formaldehyde to milk is explained by the formation of a compound which is free from the amphoteric

character of the proteid body. The carboxyl groups present, therefore, have their full value and may be titrated. The growing practice of polishing barley and peas has received considerable attention. Forster (*Z. öffentl. Chem.* **11**, 36 (1905)) shakes the suspected sample with chloroform and examines the sediment microscopically. If talc is found to be present, 5 grams of the sample are ignited and the ash fused with soda and saltpeter. The magnesium is determined in the fused residue and calculated to talc ($H_2Mg_3Si_4O_{12}$). In this way the small amount of magnesium naturally present is also considered to be derived from talc. This slight inaccuracy is avoided by Matthes and Müller (*Z. öffentl. Chem.* **11**, 76 (1905)) who shake 50 grams of the barley with water (using from 500 to 600 cc. in all), pour off the supernatant liquid after twenty-four hours, and dry and ignite the residue. The ash is examined microscopically, extracted with hydrochloric acid to remove magnesium that may have come from the outer surface of the barley, and the insoluble portion treated with hydrochloric acid and magnesium determined. Of 53 samples of rice examined by E. v. Rannier (*Z. Unters. Nahr.-Genuss.* **10**, 745 (1905)) 40 were coated with talc and 25 were also treated with a blue dye for the purpose of neutralizing the natural yellowish tint of the rice. Hefelmann (*Z. öffentl. Chem.* **11**, 309) confirms in a general way the results mentioned above. He suggests as provisional maximum limits for talc 0.3 per cent. and 0.2 per cent. for rice and barley, respectively. In several laboratories attention has been given to the study of methods for the determination of glucose and prepared foods. The fermentation methods have been studied by von Raumers (*Z. Unters. Nahr.-Genuss.* **9**, 705 (1905)) who compares the results obtained by fermenting with different varieties of yeasts. He found that compressed yeast is not suitable for this purpose because of the lack of uniformity among different varieties, leading to a corresponding lack of uniformity in the results of different laboratories. He considers that wine and fruit yeasts are not applicable because of their failure to ferment maltose, resulting in too high a figure. Of the yeasts he employed, the bottom fermentation—beer yeast—is the only one he regarded as satisfactory for this purpose. This yeast ferments maltose completely, but leaves dextrose unfermented. E. Ewers (*Z. öffentl. Chem.* **11**, 407 (1905)) recommends the quantitative determination of starch by means of the polariscope after first making the starch soluble by means of acetic acid, dilute hydrochloric acid and hot water. He finds the polarization of wheat, rice and maize starch to be equal, but that of potato starch to be somewhat higher.

FATS AND OILS BY L. M. TOLMAN.

Investigations by Winkel (*Z. Unters. Nahr.-Genuss.* **9**, 90–96 (1905)) lead to the conclusion that the changes other than ran-

cidity which take place in fat exposed to the sunlight are different from those which take place in the dark, but that in both cases the changes are due to chemical action. He also concludes that rancidity in fat is due to micro-organisms. Soltsien (*Chem. Rev. Harz. Fettind.* **12**, 177 (1905)) proposes to detect rancid butter by means of Welman's reagent, which he applies directly to uncolored butter, while with colored butters he first distils with steam and applies the test to the distillate. Klimont (*Chem. Rev. Harz. Fettind.* **12**, 160 (1905)) has reviewed the processes taking place when a fat becomes rancid. Petersen (*Chem. Ztg.* Rep. 181, 1905) has been able to change oleic acid into stearic by means of electrolysis. By dissolving 10 grams of oleic acid in 150 cc. of alcohol and adding 3 cc. of dilute sulphuric acid (1–4) and using a nickel cathode and a platinum anode in a porcelain cylinder, and passing a current of 1.35 amperes and 20 volts for four hours, the solution being kept at 30–35°, he was able to obtain a heavy precipitate of stearic acid. A number of papers on the unsaturated fatty acids and the addition (J. Moll van Charante: *Chem. Centr.* **1**, 1309 (1905)) and oxidation products (Alex. Saytzeff: *J. Pharm. Chem.* **71**, 422 (1905)) have been published. Von Molinari and Souccini (*Chem. Ztg.* 715 (1905)) have studied the action of ozone on linseed oil and found that one molecule of oleic acid absorbs three molecules of ozone while one molecule of linolic acid absorbs two molecules of ozone. This absorption the authors found to be quantitative and they propose a new number to be used in the analysis of fats to be known as the ozone number. Frank and Kamenetzky (*Chem. Centr.* **1**, 696 (1905)), *Chem. Ztg.* Rep. 75, 1905) have prepared some extensive tables of the physical and chemical constants of oils, fats and waxes. New methods for the determination of the physical constants of oils and fats have been proposed by Rakusin (*Chem. Ztg.* 841 (1905)) for the specific gravity and Ubbelohde (*Z. angew. Chemie* No. 24, 1905) for the melting-point, while Farnsteiner (*Z. Unters. Nahr.-Genuss.* **8**, 407 (1905)) has studied the index of refraction and adopts the correction for temperature change of 0.000365 for 1° C., the same as adopted by the Association of Official Agricultural Chemists in this country. Deiter (*Arb. hyg. chem. Unter.* Heft 29 (1905), in a study of the different methods for the determination of the iodine number of oils, reached the conclusion that the Hanus method was the most satisfactory and that ten to fifteen minutes was a sufficient time for the reaction to take place. The value of an examination of the unsaponifiable matter of fats has been shown by a number of investigations. On account of the effect of the food of the animal on the fat it is often impossible to place any confidence in the color tests, and the determination of the presence of phytosterol is the final test. Olig and Tillmanns (*Z. Unters. Nahr.-Genuss.* **9**, 65 (1905)) have shown, however, that the addition of a slight trace of paraffin

to the fat under examination made the phytosterol acetate test of Bomer of practically no value as the paraffin reduced the melting-point of the acetate to about 100°, but Polenske (*Arb. Kais. Ges. Amt.* **22**, 557–576) has shown that it is possible to detect this small amount of paraffin by treating the fat with strong sulphuric acid which carbonizes the fat but does not attack the paraffin. Fischer and Peyau (*Z. Unters. Nahr.- Genuss.* **9**, 81 (1905)) found that sulphurous acid would destroy the substance that gives the Halphen reaction in cottonseed oil and that the only way to detect oils treated in this way is by the phytosterol acetate method of Bomer. The Halphen test has been considered a specific test for cottonseed oil but it has been shown that Kapok and Baobab oils give the reaction which in fact seems to be characteristic of the oils of the *Malvaceae* (P. Soltsien: *Chem. Centr.* **2**, 1133 (1905)). A number of new methods for the detection of coloring-matter in fat have been proposed. Sprinkmeyer and Wagner (*Z. Unters. Nahr.- Genuss.* **9**, 958 (1905)) extract the color from a petroleum ether solution with glacial acetic acid. Arnold (*Z. Nahr.- Genuss.* **10**, 239 (1905)) uses an acid alcohol (1 cc. HCl to 99 cc. of 95 per cent. alcohol). He takes 5 cc. of the melted fat and 2 cc. of the alcohol and heats until the solutions mix. The alcohol dissolves the color and collects on the surface of the fat. Fendler (*Chem. Rev. Fett. Harzind.* 1905, 207–237) uses a mixture of nitric acid in ether as a reagent for the determination of added color. Sprinkmeyer and Wagner (*Z. Unters. Nahr.- Genuss*, **10**, 347–353 (1905)) have made a study of sesame oil and give the analyses of a number of oils from different countries. Aparin (*Zhur. Russ. Fiz. Khim. Obshch.* **36**, 581–596 (1904)) has studied the composition of the oil of the strawberry and finds it to be largely linolic and linolenic acids with only a trace of oleic acid.

DAIRY PRODUCTS BY L. M. TOLMAN.

There have been several valuable papers on the effect of the food on the composition of milk: One (Morgen C. Berger and G. Fingerling: *Landw. Vers. Stat.* **62**, 251–386 (1905)) tending to show that where the ration is normal but restricted in quantity the addition of fat and protein to the ration has a favorable effect on the milk production. Fat exerts a specific influence on the production of butter fat while protein shows no such specific action. An addition of carbohydrates to the ration was without influence on either the total yield of milk or the production of butter fat. The conclusion is drawn that food fat is especially suited to the formation of milk fat and that perhaps up to a certain limit cannot be replaced by other food constituents. Other work (T. Pfeiffer, A. Einecke and W. Schneider: *Mitt. Landw. Inst. Breslau.* **3**, 179–225 (1905)), in which such substances such as a mixture of asparagine and cane-sugar were substituted, in quan-

tities having equal fuel values, for a part of the proteids in a ration rich in proteids, showed no decrease in the quantity of milk but a lowering in the percentages of fat, protein and total solids and a decrease in the actual yield of fat, from which it is concluded that asparagine and the amides in general are not nutrients but sometimes act as stimulants to increase the yield of milk but always at the expense of the other food constituents or the body tissues. Jensen (*Landw. Jahrb. Schweiz.* **19**, 534–559 (1905); *Rev. gén. lait.* **5**, 103–110 and 121–128 (1905); **5**, 152–161, 178–185, 198–205 (1906)) calls attention to the fact that with the feeding of large quantities of saltpeter a trace of nitrate is found in the milk; that feeding large quantities of roots increased the amounts of volatile acids in the butter fat, and the feeding of sesame cake increased the content of oleic acid in the milk fat. The general conclusion of all the work is that the composition of the milk and of the milk fat is influenced to a marked degree by the food. Richmond (*Analyst*, **30**, 325–329 (1905)) gives data showing the average composition of 15,910 samples of milk. This was as follows: Specific gravity, 1.0322; total solids, 12.68 per cent.; fat, 3.75 per cent.; and solids, not fat, 8.94. As an interesting comparison with this are the results on the composition of milk of sheep by Sanna (*Staz. sper. agr. ital.* **38**, 289–306 (1905)) which shows the specific gravity to be 1.0385, total solids 18.34 per cent., fat 7.53 per cent., casein 4.65 per cent., albumin 1.01 per cent., sugar 4.05 per cent., and ash 0.89 per cent., or solids, not sugar, 10.60 per cent. The question as to the changes that take place in the composition of milk during souring is often of importance to the inspection chemist as the samples are in most cases changed before the analysis is made. In order to test this Thorpe (*Analyst* **30**, 197–205 (1905)), of the government laboratory of England, had 13 samples of fresh milk kept for periods varying from two to fourteen and one-half weeks and found that the fat content decreased on the average only 0.06 per cent. The loss of solids not fat in the same time was from 0.24 to 0.87 per cent., due mainly to the production of alcohol and volatile acids. These results show that for inspection purposes the analysis of the sour milk is satisfactory in judging the character of the fresh milk. The changes that take place in milk on sterilization and the effect of the sterilization of the milk on digestion, especially of infants, have been the subject of much study, and the results seem to show that the raw milk is more digestible although Brunon (*Bull. acad. med.* [3] **53**, 396–399 (1905)), in his report of the work of the infant milk depot at Rouen which has during the last four and one-half years fed 2,000 infants, 70 per cent. of whom suffered from malnutrition, finds that only a very few of the children failed to do well on sterilized milk. The sterilization was accomplished in an autoclave at 102° C. Jensen and Plattner (*Ann. Agr. Suisse*, **6**, 205–223 (1905) *Rev. gén. lait.* **4**, 361–368, 388–397,

419–424 (1905)), in an extensive study of the effects of heating milk for various lengths of time and at different temperatures found that marked changes took place in the chemical composition of the milk, and concluded from their work that in order to retain the properties of the raw milk the heating in sterilization should not exceed 70° C., which is sufficient to destroy pathogenic bacteria.

O. Laxa (*Milchw. Zentbl.* **1**, 538–547 (1905)), in a study of casein and paracasein, finds that lactic acid unites with casein to form lactates and that under the influence of acids paracasein changes to casein. He found that lactates that contained 1 per cent. or less of lactic acid were insoluble in water while those of higher content were soluble. He was able to prepare lactates that contained as high as 7.5 per cent. of acid. He concludes that the monolactates and dilactates of Van Slyke and Hart are untenable, a conclusion that these authors have reached in their later work. He explains the curdling of milk by the formation of lactic acid which changes the phosphates of the milk into acid salts and the precipitation of the soluble lactates by the mineral acid. Laquer (Abs. in *Osterr. Chem. Ztg.* **8**, 521 (1905)) found that paracasein contained more carbon and hydrogen than casein but 0.8 per cent. less nitrogen, that it had the same acidity as casein but was more readily precipitated by salts. Porcher (*Compt. rend.* **141**, 73–75 and 467–469 (1905)), as the result of his studies on the physiology of the mammary gland, concludes that the transformation of glucose into lactose is a function of this gland. Methods for the estimation of fat in milk have been the subject of a great deal of study during the last year. The Gottlieb-Rose or the Sichler "sin-acid" methods both seem to be very promising. A number of chemists have given the Gottlieb-Rose method a thorough trial in comparison with the standard methods and have in all cases found it to give reliable results. Thomsen (*Mealkeritid.* **18**, 356–359 (1905)) showed that it was not necessary to peptonize the milk to obtain complete extraction with the Gottlieb-Rose method while unless this is done with the ordinary method of ether extraction low results are obtained. Burr (*Z. Unters. Nahr.- Genuss.* **10**, 286–290 (1905)) considers that the method is applicable to all dairy products. The results on the "sin-acid" method of Sichler have not been so uniform, some chemists finding it as satisfactory (Lotterhos: *Molk. Ztg.* **19**, 145–146 (1905)) as the Gerber method and others not entirely satisfactory (M. Klassert: *Z. Unters. Nahr.- Genuss.* **9**, 12–15 (1905)). Unfortunately, the reagent used in this test is a secret so that the application and improvement of the method is likely to be slow. The advantage of a method, which does not use an acid to dissolve the proteids of the milk, as is the case in the Gerber and Babcock methods, in the analysis of such products as sweetened condensed milk where the acid chars the cane-sugar so that the

method is not applicable, can be readily seen. The use of a fine sponge as the absorbent material in milk analysis has been tried by Bellier (*Ann. chim. analyt.* **10**, 268–276 (1905)) with success. The sponge was first extracted with dilute hydrochloric acid, alcohol, ether and water and dried. The weight of the sponge prepared in this way remains practically constant. The milk is transferred to the sponge and dried to constant weight, extracted with ether for the fat, treated with formaldehyde to render the proteids insoluble, this is washed with 50 per cent. alcohol containing 5 per cent. of acetic acid and water to remove the sugar and ash thus giving him a complete analysis of the milk on one sample. Another ingenious method has (F. Bordas and Touplain: *Ann. chim. analyt.* **10**, 267–268 (1905); *Rev. soc. sci. hyg. aliment.* **2**, 163–168 (1905)) been proposed for making an analysis of milk on a single portion; 10 cc. of milk are added drop by drop to a centrifuge tube containing 25 cc. of 65 per cent. alcohol acidified with acetic acid and after standing for a few minutes the tube is whirled. The supernatant liquid is poured off and the sugar determined in it. The residue in the tube is extracted with ether several times, whirling each time to settle the insoluble material and decanting the ether, which is evaporated and weighed. The residue in the tube is dried and weighed as casein. The detection of added water in milk is one of the most important determinations that the chemist has to make in the inspection of milk supplies, and the specific gravity and index of refraction of the milk serum have been found of great value in detecting this form of adulteration. Bialon (*Milchw. Zentbl.* **1**, 499–502 (1905)) has shown that the method employed in preparing the serum makes considerable difference in its specific gravity. In one case the serum obtained by spontaneous coagulation had a specific gravity of 1.0284, that where acetic acid was used 1.0266, and that prepared by rennet 1.0291. This he explains by the different amounts of phosphates, lime, and proteids left in solution. The serums prepared by the same method did not give uniform results and better results were obtained by the following formula:

$$\sigma = \frac{100\,s - f}{100 - \frac{f}{0.933}}$$

in which s represents the specific gravity of the milk, f the percentage of fat, and 0.933 the average specific gravity of milk fat. For pure milk σ or the specific gravity of the fat-free milk was found to be about 1.0323. On the basis of a large number of determinations, the author concludes that a specific gravity of 1.0323 or above calculated by this formula shows that the milk is unadulterated, while a lower figure shows that water has been added. The method is, of course, not applicable to curdled milk.

This difference in the serum would affect the results by the index

of refraction in the same way. The best method of preparing the serum, according to Henseval and Mullie (*Rev. gén. lait.* **4**, 529–538 (1905)), is to add 1 cc. of 20 per cent. acetic acid to 50 cc. of the milk, heat on a water-bath to 65–70° for five minutes, cool to 15°, filter, read the index of refraction at room temperature and calculate to 15° by the factor 0.000117 for each degree centrigrade. The same result has been attempted by the determination of the freezing-point of the milk and a number of chemists have obtained very uniform figures for this test. Allermann (*Landw. Jahr.* **19**, 499–502 (1905)) found that the average freezing-point of 23 samples of milk was —0.571° C., Barthel (*Rev. gén. lait.* **4**, 505–512 (1905)) found it to be very constant between —0.55° and —0.57° C. Bomstein (*Russ. Vrach.* **3**, 3 (1905)) claims to be able to detect 5 per cent. of added water and Lajoux (*Ann. chim. anal.* **10**, 210–231 (1905)), from his work, suggests a standard for market milk of —0.55° to 0.57°. It must be remembered, however, that such substances as glycerol (*Ann. chim. anal.* **10**, 89–90 (1905)), sodium bicarbonate and formalin influence these results very much. The presence of nitrates in the milk as a test for added water is not always (J. Adorjan: *Z. landw. Vers. Oesterr.* **8**, 846–851 (1905)) to be relied on as a little dirt in the milk or the water used in washing the cans may cause the milk to give the reaction. The presence of ammonia in milk (Trillat and Sauton: *Ann. inst. Pasteur.* **19**, 494–502 (1905)) is also an indication of added water and may be detected by the nitrogen iodide test as follows: Ten cc. of the milk are placed in a test-tube and treated with 10 cc. of a 10 per cent. solution of iodine trichloride. The filtrate is carefully neutralized with lime water; when in the presence of ammonia a black precipitate of nitrogen iodide soluble in an excess of the reagent is formed. The value of a preservative which does not change the amount of solids or ash in the milk for preventing changes in milk kept for analysis is evident and some results by Hoft (*Chem. Ztg.* **29**, 54 (1905)) show that formalin to the extent of 4 drops to 100 cc. does not affect the percentage of solids, but larger amounts cause an appreciable increase. Seligmann (*Z. Hyg. Infectionskrank.* **49**, 325–328 (1905)) proposes the use of Schiff's reagent for the detection of formalin in milk. He adds 2 to 3 drops of sulphuric acid to 5 cc. of the milk and then adds the reagent which gives a violet-red color in the presence of as little as 1:40,000. Utz (*Milchw. Zentbl.* **1**, 175–178 (1905)) detects the presence of hydrogen peroxide in milk by the use of titanic and vanadic acids.

The collection of data as to the variability of the composition of butter fat shows two reports on Holland butter: one, that of Van Sillevoldt (Abs. in *Z. Unters. Nahr.-Genuss.* **9**, 734 (1905)) gives out of 3945 samples examined during January, February and March, only 4 samples that had a Reichert-Meissl number under 24, while in the three months preceding, 32 samples fell

below, while Bemelman's report (*Contribution à l'étude de la variabilité des constantes des beurres néerlandais. Bréda*, 1905, pp. 81; Abs. in *Rev. gén. lait.* **4** No. 22, pp. 521–522 (1905)), on the butter of 485 Holland cows shows that the Reichert-Meissl number quite generally fell below 24.

The question whether feeding sesame cake to cows will cause the butter to give the Baudoin reaction is of great importance in countries which require that sesame oil shall be added to oleomargarine. Denoel (*Bull. Agr.* (Brussels) **21**, 183–192 (1905)), in some recent experiments, was unable to find a trace of a test in the butter from cows fed on sesame cake. This is contrary to the results of many other experiments, and to what might be expected from the results that have been obtained by feeding cottonseed meal. The detection of cocoanut oil in butter has received a good deal of attention. Jensen (*Landw. Jahrb. Schweiz*, **19**, 477–495 (1905); *Ann. Agr. Suisse*, **6**, 224–246 (1905); *Rev. gén. lait.* **4**, 437–447, 457–464, 481–490 (1905)) has studied the volatile acids of cocoanut oil and of butter fat and finds that cocoanut oil contains no butyric and very little caproic acid, while butter on the average contains 3.92 per cent. butyric and 1.88 per cent. of caproic acid. Kirshner (*Z. Unters. Nahr.-Genuss.* **9**, 65–70 (1905)) applies this work of Jensen and separates the caprylic acid which is the chief acid of cocoanut oil from the butyric acid by the use of its silver salts.

An interesting paper by Eckles and Rahn (*Centr. Bakt.* **14**, 676–680 (1905)), on the changes taking place in Hartz cheese, shows that of the total nitrogen in the ripe cheese 86.2 per cent. is in the form of albumoses and peptones, 6.7 per cent. exists as amides, 3.5 per cent. as ammonia, and 3.6 per cent. as insoluble proteids, showing a much higher percentage of water-soluble proteids than occurs in Camembert and other kinds of cheese. The changes taking place in Edam cheese in the process of ripening have been studied (F. W. J. Boekhout and J. J. O. de Vries: *Centr. Bakt.* 2 *Abt.*, **15**, 321–334 (1905)) and the amount of insoluble lime is considered of great importance.

NEW BOOKS.

GENERAL INORGANIC CHEMISTRY. By ALEXANDER SMITH. New York: The Century Co. 1906. xviii+780 pp. Price, $2.25.

It is a difficult, if not impossible, task to give, within the bounds of a review, an even approximately adequate idea and criticism of this comprehensive and important text on general chemistry.

Professor Smith has succeeded in including in his book, of comparatively small external dimensions, all that is given in the largest college texts on descriptive, inorganic chemistry, and a

fairly complete course on elementary physical chemistry as well. This has been accomplished by a rare combination of conciseness of expression with such good judgment that nothing essential for clearness is omitted. It is not too much to say that every one of the 766 pages of text shows unmistakable evidence of careful deliberation and of original thought. No one could fail to recognize that it must have taken years to compile this book and to weld it into one homogeneous whole, even though the author had not stated in his preface that "the first draft was written six years ago" and that it is the outgrowth of a course in chemistry which he has given for fifteen years.

It is natural, in fact inevitable, to compare this book with the translation of Ostwald's "Grundlinien." In spite of the difference in size, the two contain practically the same number of pages, the same amount of information on a page, and about the same subjects. It is evident that Smith agrees in the main with Ostwald in what should be taught, and in how to teach it, but there is no trace of plagiarism or even of imitation. Such close correspondences as occur result from the fact that there is but one best way to present certain subjects, and Smith has ample grounds to trust to the merits of his own work and not adopt some other way merely to create a deceptive atmosphere of novelty.

The book is full of suggestions and of pithy phrases, valuable to teachers as well as students. For instance, objection is offered to the common expression a "gas disobeys the law." Smith says: "Our procedure, in such cases, is always more logical than our language, for we never attempt to cure a gas of its error, but always the law itself by suitable modification in its phraseology." Again: "There is no such thing as a final explanation. An explanation in science never professes for a moment to give the reasons for any occurrence. We simply don't know why behavior in nature is as it is," and he defines explanation as, "a description in greater detail." He relegates the familiar statement "the mass of the universe is a constant" to metaphysics, as something transcending experience. He makes some statements, notably in his definitions, "an element is....a kind of matter which never exists alone," and "a simple substance....contains but one element combined with a certain quantity of energy," which smack enough of metaphysics to be questionable, judging them according to his own standard. The objection to the term

chemical equation, and the substitution of a single arrow for the equality mark is an innovation which the reviewer frankly doesn't like. On page 55 we read, "....the chemical equation is not an algebraic expression; it is subject to none of the rules of algebra." But on page 78 two equations are added, and terms common to both sides are canceled, as is the universal custom in handling energy equations.

It is worthy of particular notice that the chapter on the atomic hypothesis begins on page 217. One must study the book to realize how much chemistry the student is required to learn before he is trusted with this useful but dangerous implement of thought. In this portion of the book the author is at his best, developing a caustic humor, a terseness and an effective sarcasm, which makes more interesting reading than a novel. It is impossible to refrain from an illustrative quotation. "The egregious misconception that sulphuric acid is shown by this action to be 'stronger' than hydrochloric acid was disposed of, so far as the science was concerned, half a century ago. But it survives in suburban chemical circles with remarkable tenacity." It would be a fascinating occupation to discuss the book in detail, quoting many of the characteristic and clever expressions, but space forbids.

The first 530 pages are devoted to the non-metallic elements and the general principles, and the last 236 pages to the metals. The description of potassium is begun on page 548. This does not mean that the metals are neglected by any means. They are as thoroughly treated as one could wish. There is more on steel than in any other book for beginners. But the distribution of the available space and time is what is significant, illustrating the change which has been necessitated in the teaching of beginning chemistry in recent years owing to the introduction of so many fundamental, valuable, indeed indispensable principles and theories which comprise what is well named general chemistry, what might perhaps even better be called universal chemistry (translating literally the German 'Allgemeine Chemie'), because they find application in every branch of the science to-day. Many, educated under the old régime, are unable to understand why the progress of the first course is so slow when measured in terms of the number of substances taken up. A careful perusal of this book would go far to explain the phenomenon to them.

Misprints are remarkably few in number and insignificant in kind. The absence of these faults, so common in a first edition, is but another indication of what is apparent throughout, that no labor has been spared. It is therefore surprising that the index is deplorably poor. When one finds "sulphocyanates, see thiocyanates" and then finds "thio-, see sulpho-" he is apt to become discouraged. Moreover, it ought to contain at least twice as many titles as it does, to facilitate reference to the great quantities of information. It is to be hoped that the second edition, which will probably not be long in coming, will contain an index worthy of the rest of the book.

It is a serious question whether Smith has not carried a good thing a little too far, whether he has not, after all, developed his general physical chemical principles beyond what is advisable for beginners. For example, the mathematical expression of Ostwald's dilution law and the integrated expressions for reactions of the first and second order, to determine the reaction constants, really belong in a more advanced course. In the opinion of the reviewer the book contains somewhat more than the maximum amount of information which can be introduced into the minds of the average university Freshman in a course consisting of three lectures and two two-hour laboratory periods a week extending through one college year. But the use of large type for the most important portions, and of small type for the less important, the prominent headings, the summaries of principles and the lists of questions and problems at the ends of chapters, will make it easy to select topics and utilize the book in shorter courses.

For some, the adoption of this book will necessitate a thoroughgoing revision of lectures, and a good deal of hard work. But it is to be hoped, for the sake of the subject of chemistry, that this may not delay its coming into general use. The reviewer gladly acknowledges that he has derived much profit from the careful study which he has given the book. It is a most admirable text and one destined to become a standard.

S. LAWRENCE BIGELOW.

AN ELEMENTARY LABORATORY COURSE IN CHEMISTRY. By FRANK B. KENRICK, Lecturer in Chemistry, and RALPH E. DE LURY, Fellow in Chemistry, University of Toronto. Toronto: Morang & Co. 1905. vi+90 pp. Price, $1.00.

"The course of Practical Chemistry outlined in this book is

intended for students who are beginning the subject and.... [are] taking a course of lectures on general chemistry." The titles of the main sections are as follows: Solution and Crystallization; Separation by Solution; Experiments with Air; Combustion of Magnesium; Properties of Magnesium Oxide; Chemical Substances; Composition of Water; Weight of Hydrogen Evolved when Magnesium Dissolves in an Acid; Law of Reacting Weights; Properties and Composition of Acids; Acids, Bases and Salts; Solubility; Separation by Volatilization; Properties of Aqueous Salt Solutions; Quantitative Separation by Solution; Precipitation of Copper; Proportion of Copper in Copper Oxide; Chemical Reaction in Solution; Measurement of Liquids; Volumetric Analysis; Law of Reacting Weights in Solution; Volume Relations of Gases; Some Experiments to Illustrate the Influence of Conditions on Reactions; A Reversible Reaction; The Mass Law; Applications of the Mass Law; Dissociation of Salts in Water; Some Experiments on Dissociation; Application of Mass Law to Dissociation; Separation and Identification of Substances; Solubility Tables; Principles of Qualitative Analysis; Separation of "Group I;" Separation of "Group II B;" Analysis of a Silver Coin.

Part II deals with elementary qualitative analysis, and in an appendix some additional explanatory paragraphs, containing also a few experiments, are given.

The old style of laboratory manual dealt almost exclusively with descriptive chemistry, and the work based upon it contributed nothing to the student's knowledge of the laws and principles of chemistry and therefore little to his mastery of the subject as a science. The great majority of existing manuals are still of this one-sided kind. A few make a more or less definite attempt to teach the science as it is. The present work is noteworthy in that, as may be seen from the titles of the chapters, it is arranged entirely with a view to emphasizing the principles of experimental chemistry. Much of the subject-matter of descriptive chemistry will be found in it—more than forms the whole content of many other manuals—but it is all arranged primarily to illustrate the principles. The directions, remarks, and questions, which, with the practical work and the head work of the pupil that they demand, constitute a clear study of each topic, are all elaborated with an admirable ingenuity which leaves nothing to be desired. Teachers of general inorganic

chemistry will find the book a most instructive and suggestive one.

In matters of detail some criticisms will occur to the reader. For example, the quantitative experiments on the composition of water and on the weight of hydrogen displaced by a given weight of magnesium give, in the hands of beginners, results so inaccurate that their usefulness is thereby largely destroyed. Again it is unfortunate that arbitrary words like *hydrogenion*, *cupricion*, and *leadion* should be employed when a logical system like Walker's is already in use by chemists. But these details do not materially obscure the very pronounced merits of the book. A. S.

THE CHEMISTRY OF PAINTS AND PAINT VEHICLES. By CLARE H. HALL, B.S. New York: D. Van Nostrand Co. 1906. 134 pp. Price, $2.00.

This is a book written by a chemist engaged in the manufacture of paints and colors, and gives what, in the judgment of the author, are the best methods for determining the various substances which practically occur in ordinary paints. As a rule only one method is given for each substance, and a good working knowledge of analytical methods is assumed. The book would be better if more details were given, or if there were references to standard works; but on the whole it may be said that the book is useful, indeed valuable, to any one engaged in such work. Probably any other chemist will believe some method not given here better than the one given; but by being rigidly confined to one method for each substance, the book is made compact and intelligible. In the judgment of the reviewer, some valuable methods are omitted, *e. g.*, McIlhiney's method for separating turpentine, etc., and the use of the polariscope and refractometer in detecting adulterations in liquids; also Langmuir's method for shellac. On the whole, the book is a good book and would be better if there were more of it. The most common failing of the specialist is that of forgetting that what is well-known to him is not familiar to his readers; because no book is written for specialists only. A. H. SABIN.

RECENT PUBLICATIONS.

ELECTROCHEMISTRY OF ORGANIC COMPOUNDS. By Walther Löb. Trans. from the author's enlarged and revised third edition by H. W. F. Lorenz. New York: J. Wiley & Sons. 1906. 10+308 pp. $3.00.

INTRODUCTION TO GENERAL INORGANIC CHEMISTRY. By Alexander Smith. New York: Century Co. 1906. 18+780 pp. $2.25.

ELECTRICAL NATURE OF MATTER AND RADIOACTIVITY. By Harry C. Jones. New York: D. Van Nostrand Co. 1906. 9+212 pp. $2.00.

GLUES AND CEMENTS. HANDBOOK ON ADHESIVES AND FILLINGS FOR WORKSHOP USE. By H. J. S. Cassal. London: L. U. Gill. 1906. 102 pp. 1/.

FOOD PRESERVATIVES. By R. G. Eccles. London: K. Paul. 1906. 5/.

ARCHITECTURAL HARDWOOD FINISHING: A PRACTICAL TREATISE ON MODERN METHODS OF FINISHING THE WOOD OF NEW BUILDINGS. By G. Whigelt. New York: Painters' Magazine. 1906. 124 pp. $1.00.

LOGARITHMISCHE RECHENTAFELN FÜR CHEMIKER, PHARMAZEUTEN, MEDIZINER UND PHYSIKER. By F. W. Küster. Sixth edition. Leipzig: Veit & Co. 1906. 99 pp. Marks 2.

HANDBUCH DER SEIFENFABRIKATION. By G. Deite. 1. Bd. Hausseifen und Textilseifen. Third edition. Berlin: J. Springer & Co. 1906. 12+633 pp. Marks 10.

THEORIE UND PRAXIS DER GARNFÄRBEREI MIT DEN AZO-ENTWICKLERN. By Dr. Franz Erban. Berlin: J. Springer. 1906. 14+485 pp. Marks 12.

HANDBUCH DER BAUMWOLLE-INDUSTRIE. By Ernst Fränk. Berlin: Verlag für Textil-Industrie. 7+196 pp. Marks 5.

UEBER DIE DEDUKTION DER STÖCHIOMETRISCHEN GESETZE. By Carl Benedicks. (Berlin: R. Friedländer & Sohn.) 1906. 14 pp. Mark 0.80.

GRUNDRISS EINER ENTWICKLUNGSGESCHICHTE DER CHEMISCHEN ATOMISTIK ZUGLEICH EINFÜHRUNG IN DAS STUDIUM DER GESCHICHTE DER CHEMIE. By Rich. Ehrenfeld. Heidelberg: C. Winter. 1906. 8+314 pp. Marks 8.

LEHRBUCH DER CHEMIE. AUTORIS. DEUTSCHE AUSG. LEHRBUCH DER UNORGANISCHE CHEMIE FÜR STUDIERENDE. By A. F. Holleman. Fourth edition. Leipzig: Veit & Co. 1906. 12+451 pp. Marks 10.

CHEMISCHE PRAKTIKUM FÜR NATURWISSENSCHAFTLER. By M. Dittrich. Heidelberg: C. Winter. Marks 4.50.

HANDBUCH DER FARBEN-FABRIKATION. LEHRBUCH DER FABRIKATION. By George Zerr and R. Rubencamp. Dresden: Steinkopff & Springer. 1906. 12+850 pp. Marks 27.

MANUAL OF TOILET SOAP-MAKING. By C. Deite. New York: D. Van Nostrand Co. 1906. 147 pp. $5.00.

CHEMISTRY OF PAINT AND PAINT VEHICLES. By Clare H. Hall. New York: D. Van Nostrand Co. 1906. 115 pp. $2.00.

CHEMISTRY SIMPLIFIED. By G. A. Koenig. Phila: D. Van Nostrand Co. 430 pp. $2.25.

NOTES ON VOLUMETRIC ANALYSIS. By J. B. Russell. New edition. New York: Dutton & Co. 1906. 8+94 pp. $0.30.

FOOD INSPECTOR'S HANDBOOK. By Francis Vacher. Fourth edition. New York: D. Van Nostrand Co. 1905. 16+231 pp. $1.50.

CHEMISCHE UND PHYSIKALISCH-CHEMISCHE UNTERSUCHUNG DER LINDENQUELLE ZU BIRRESBORN IN DIE EIFEL. NEBST UNTERSUCHUNG ÜBER DEREN RADIOAKTIVITÄT. By Ernst Hintz. Wiesbaden: C. W. Kreidel. 1906. 45 pp. Marks 1.20.

CHEMISCHE UND PHYSIKALISCH-CHEMISCHE UNTERSUCHUNG DER SALZTRINK

QUELLE ZU BAD PYRMONT. By Ernst Hintz. Wiesbaden: C. W. Kreidel. 1905. 45 pp. Marks 1.20.

KURZES REPERTORIUM DER ORGANISCHEN CHEMIE. By K. Dammann. Freiberg i/B. Herder. Marks 4.

ANALYSE CHIMIQUE INDUSTRIELLE. By G. Lunge. Trans. by E. Campagne. Tome 1, Industrie minérales. Paris: Ch. Béranger. 640 pp. 22 fr. 50.

L'OXYGÈNE ET L'OZONE. LES ACIDES MINERAUX, L'AMMONIAQUE, LES VITRIOLS, LES ALUMS. By H. Pecheux. Paris: J. B. Baillière et fils. 96 pp. 1 fr. 50.

LES NOUVEAUTÉS CHIMIQUES POUR 1906. By Poulenc. Paris: J. B. Baillière et fils. 314 pp. 4 fr.

INTRODUCTION TO CHEMICAL CRYSTALLOGRAPHY. By P. Groth. Trans. by Hugh Marshall. London: Gurney. 1906. 136 pp. 4/.

BERICHT DER INTERNATIONALEN ANALYSEN-KOMMISSION AN DEM VI. INTERNATIONALEN KONGRESS F. ANGEWANDTE CHEMIE IN ROM, 1906. (IN DEUTSCHER, FRANZÖS. UND ENGL. SPRACHE.) By G. Lunge. Zurich: Zurcher & Furrer. 1906. 6+421 pp. Marks 10.

ANALYSE DES MÉTAUX PAR ELECTROLYSE. By A. Hollard and L. Bertiaux. Paris: Ch. Béranger. 184 pp. 6 fr.

QUALITATIVE BOTANISCHE ANALYSE DER DROGENPULVER. EINE EINFÜHRUNG IN DEN GANG EINE SYSTEMAT. MIKROSKOP. PULVERUNTERSUCHUNG. By P. Schürhoff. Berlin: J. Springer & Co. 1906. 6+9 pp. Marks 2.

ABRISS DER ALLGEMEINEN ODER PHYSIKALISCHEN CHEMIE. ALS EINFÜHRUNG IN DIE ANSCHAUUNGEN DER MODERNEN CHEMIE. By Carl Arnold. Second edition. Hamburg: L. Voss. 1906. 8+228 pp. Marks 3.75.

HANDBUCH DER ANGEWANDTEN PHYSIKALISCHEN CHEMIE IN EINZELDARSTELLUNGEN. *3. Bd. MASCHINENKUNDE FÜR CHEMIKER. By Reg.-R. Ihering. **4. Bd. Theorie der Verdampfung. By J. P. Kuenen. Leipzig: J. A. Barth. 1906. 8+396: 12+244 pp. *Marks 15. **Marks 13.

ELEKTROLYSE GESCHMOLZENER SALZE. By Richard Lorenz. 3. Thl. Elektromotorische Kraft. Halle: W. Knapp. 1906. 18+322 pp. Marks 10.

TECHNOLOGIE DER PAPIERFABRIKATION. By Eduard Engländer. Wien: F. Deuticke. 1906. 54 pp. Marks 1.

PRINCIPES DE CHIMIE. NOMENCLATURE, NOTATION ATOMIQUE. By H. G. Bonnin. Tours: Author. 32 pp. 1 fr.

CHEMISTRY OF HAT MANUFACTURING. LECTURES DELIVERED BEFORE THE HAT MANUFACTURERS' ASSOCIATION. By W. Smith. London: Scott, Greenwood. 1906. 132 pp. 7/6.

PRACTICUM DER PHYSIOLOGISCHEN UND PATHOLOGISCHEN CHEMIE NEBST ANLEITUNG ZUR ANORGANISCHEN ANALYSE FÜR MEDICINER. By E. Salkowski. Third edition. Berlin: A. Hirschwald. 1906. 13+315 pp. Marks 8.

SPEKTROSKOPISCHE UNTERSUCHUNG DER TERBIUMPRÄPARATE V. DR. G. URBAIN. By G. Eberhard. Berlin: G. Reimer. 1906. 21 pp. Mark 1.

BEITRAG ZUR STEREOCHEMIE DER 2,5-DIKETOPIPERAZINE. By Emil Fischer and Karl Raske. Berlin: G. Reimer. 1906. 13 pp. Mark 60.

ANILINFARBEN UND IHRE FABRIKATION. By K. Heumann. IV. Thl. Hrsg. von Gust. Schultz. 2. Hälfte. 2. Abthlgn. Braunschweig: F. Vieweg & Sohn. 1906. 7,5 und pp. 1041–2595. Marks 50. Geb. Marks 56.

LIST OF BOOKS ON CERAMICS. Free Public Library of the City of Trenton, N. J.